



Review

Advances in the synthesis of bismuth-based heterojunction photocatalysts and visible light photodegradation of ciprofloxacin and levofloxacin in aqueous solutions: Degradation efficiency, degradation products, and their toxicity

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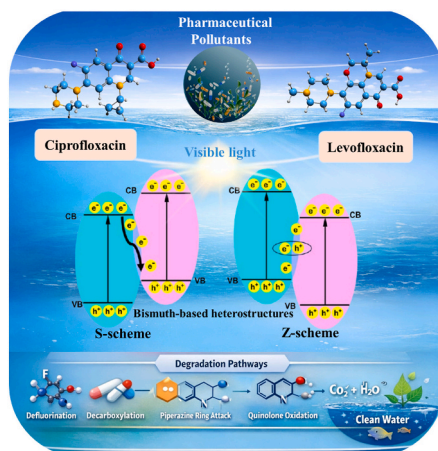
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HIGHLIGHTS

- Ciprofloxacin and levofloxacin are the two most commonly found antibiotics in water.
- This review covered bismuth-based heterojunctions studied for their photodegradation.
- The photodegradation performance of heterojunctions was compiled and compared.
- Degradation mechanisms of various heterojunctions were outlined.
- The degradation paths, degraded products, and their possible toxic effects discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Antibiotic pollution in water systems is a critical global challenge that worsens the global water scarcity crisis by contaminating vital freshwater reserves and creating dangerous antimicrobial resistance. Photocatalysis uses solar energy to power green catalytic treatments that clean antibiotic-contaminated water by breaking down persistent pharmaceuticals without using any harsh chemicals. Bismuth-based heterojunction photocatalysts leverage heterojunction engineering that drastically improves charge carrier separation and minimizes electron-hole recombination while enhancing redox potential for the destruction of environmental pollutants. In this article, we reviewed the removal of levofloxacin (LEV) and ciprofloxacin (CIP), the two most detected antibiotics in wastewater and aquatic environments globally, by various bismuth-based heterojunctions. Their photodegradation performance has been compiled and compared, and possible degradation routes, photodegradation

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mechanisms, and ecotoxicity of the degraded products are discussed. A true comparison of the degradation performance of CIP and LEV by various heterojunctions is difficult because various light sources, radiation intensity, pollutant concentration, and catalyst dose were used in various published studies. Of the heterojunctions so far developed, $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{WO}_6$ and $\text{Bi}_2\text{O}_3/(\text{BiO})_2\text{CO}_3$ showed excellent CIP removal, and their photodegradation rate constants were 0.5571 and 0.476 min^{-1} , respectively. Conversely, for the removal of LEV, $\text{Bi}_2\text{WO}_6/\text{CuS}$ and $\text{BiOCl}/\text{Bi}_2\text{Fe}_4\text{O}_9$ provided excellent photodegradation, and the rate constants were 0.2639 and 0.0934 min^{-1} , respectively. Toxicity analyses show that many degradation intermediates of CIP and LEV are toxic and mutagenic if the photodegradation is incomplete. The development of low-cost photocatalytic drug removal technology based on bismuth-based heterojunctions holds significant potential to make drinking water safer for human and animal consumption.

1. Introduction

The lack of sufficient, accessible water resources to meet demand affects over two billion people worldwide. The water demand in those parts of the world exceeds its availability, affecting both humans and ecosystems. Water quality and aquatic ecosystems are severely affected, driven by climate change, population growth, and anthropogenic activities, primarily from industrial discharge, agricultural runoff, and untreated municipal sewage. Key pollutants include heavy metals (e.g., copper, mercury, lead), nutrients (e.g., phosphorus), pharmaceutical drugs (antibiotics), fertilizers, and textile dyes. The release of various organic and inorganic toxins from different industries into the ecosystem without adequate treatment causes contamination of not only the surface water but also the groundwater. Antibiotics are increasingly recognized as critical emerging environmental pollutants driven by increased human consumption, veterinary use, and manufacturing. Their persistence in the environment accelerates the spread of antimicrobial resistance, threatening global human health and safety. A recent study reported that over 40% of the tested rivers potentially contained harmful levels of pharmaceutical residues, often exceeding safety limits (Rusu et al., 2023). Moreover, pharmaceutical residues disrupt aquatic life, leading to endocrine disruption in fish and increased susceptibility to predation (Obinna et al., 2023). The long-term consumption of antibiotic-contaminated water has several implications for human health, such as direct toxic effects on human organs, disruption of the body's natural microbiome, and, more seriously, the development of antibacterial resistance.

Ciprofloxacin (CIP) and levofloxacin (LEV), two of the most widely used second-generation fluoroquinolone antibiotics, are frequently prescribed for a broad range of infections (da Silva Bruckmann et al., 2025). Their use recently increased due to their better effectiveness in killing a wider range of bacteria, including those resistant to older-generation penicillin drugs (Fàbrega et al., 2008), resulting in an increase in the manufacturing of CIP and LEV to 239.14 tons and 93.94 tons per annum, respectively (Lopes et al., 2024). They are predominantly eliminated from the human body through the kidneys mostly unchanged (Baum et al., 2013), and because of untreated or poorly treated sewage systems in many regions, they can end up in aquatic systems (Diniz et al., 2021). They are considered a 'pseudo-persistent' pollutant (Wu et al., 2024), as they are constantly introduced into the environment faster than they can be degraded. Other than their effects on humans, they are environmentally hazardous due to their toxicity toward aquatic organisms (Pauletto and De Liguoro, 2024). For example, the EC_{50} value for CIP against *Daphnia magna* and *Raphidocelis subcapitata* (green algae) is below 0.01 and 0.0033 mg/L, respectively (González-Pleiter et al., 2013).

Recently, bismuth-based hetero-junction photocatalysts were found to be highly effective for the removal of these two drugs from water by solar/visible light photodegradation (da Silva Bruckmann et al., 2025; Cruz-Filho et al., 2024). However, their photodegradation pathways and the toxicity of the photodegradation products deserve more careful observation, as many degradation products show toxicity ranging from low to high. Several published articles have reviewed the degradation of various water pollutants by bismuth-based heterojunctions (Chowdhury

et al., 2025; Ain et al., 2025; Orimolade et al., 2026). However, none of them have made a mechanistic comparison of the degradation performance of various heterojunction photocatalysts, nor have they discussed a unified framework mapping the relationship between heterojunction architecture, the regulation of reactive species, and the resulting degradation pathways. Moreover, none discussed photodegradation routes of LEV and CIP by bismuth-based heterojunctions, degradation products of antibiotics, toxicity of degraded products, and the regeneration and recovery of such catalysts. This review article covers the fundamentals of heterojunction photocatalysts, synthesis methods, and their application for the removal of CIP and LEV, and compiles and compares their photodegradation performance, photodegradation mechanisms, reaction kinetic models, and regeneration of spent photocatalysts. The photodegradation routes and degradation products of LEV and CIP by various bismuth-based heterojunctions, and the toxicity of the degradation products are outlined. This review article is timely and highly valuable due to the rapid growth of scientific research in this area and the superior performance of these heterojunction photocatalysts.

2. Fundamentals and types of heterogeneous ternary heterojunctions

2.1. Fundamentals of heterogeneous ternary heterojunctions

Heterojunction catalysts are advanced materials consisting of junctions between two or more different semiconductors with unequal band structures or a semiconductor and a metal. They are designed to drastically improve the efficiency of solar-to-chemical energy conversion by resolving the main limitation of single-component semiconductors, which is rapid charge recombination. The performance of a heterojunction photocatalyst strongly depends on the band alignment at the interface. By engineering the interface, these catalysts optimize charge separation, expand light absorption ranges, and create synergistic effects that boost activity, stability, and selectivity compared to single-component catalysts (Yaw et al., 2025; Zhang et al., 2022). They operate through tailored band structures (valence and conduction bands) at the interface, allowing for efficient spatial separation of photo-generated charge carriers (electrons and holes). They have tunable properties, along with the ability to absorb a broadened spectrum of light and enhanced charge transfer with reduced recombination rates, increasing their photodegradation efficiency. Based on the electronic affinity and energy band structure of semiconductors, conventional heterostructures can have Type I, Type II, and Type III band alignments. Recently, some other heterojunctions, such as S-Scheme, Z-Scheme, p-n, and Schottky junctions, have been developed. Photocatalytic heterojunctions are categorized by their charge-transfer mechanisms, moving from modern, high-efficiency designs (e.g., S-Scheme, Z-Scheme, and p-n type) to conventional or less-effective configurations (e.g., Type II, Type I, and Type III).

2.2. Types of semiconductor heterojunctions

2.2.1. S-scheme

An S-scheme heterojunction is an advanced twin-component

semiconductor interface and is designed to enhance solar energy conversion by using an internal electric field to destroy weak charge carriers, maximize redox ability, and suppress electron-hole recombination. S-scheme heterojunctions consist of a reduction semiconductor (RP) and an oxidation semiconductor (OP) that form an internal electric field to separate charges while retaining high-energy electrons in the RP's conduction band and holes in the OP's valence band (Resasco et al., 2016). When the RP (smaller work function, high Fermi level) and OP (higher work function, low Fermi level) make contact, electrons move from the RP to the OP, creating a built-in electric field, band bending, and an electron depletion layer in the OP and electron accumulation in the RP (Fig. 1a). These junctions are frequently classified by the dimensionality of their components, with 2D materials acting as versatile scaffolds for other 0D, 1D, or 2D materials, often utilizing inorganic semiconductors or organic-inorganic combinations (Ma et al., 2026). Unlike Type-II junctions, which often reduce redox power by forcing electrons and holes to migrate to lower-energy bands, S-schemes retain strong oxidation and reduction potentials by recombining low-potential charge carriers, ensuring that only high-potential charge carriers participate in reactions (Tu et al., 2024). They do not require a shuttle redox mediator like a Z-scheme heterojunction to effectively separate charge carriers (Chen et al., 2024a). RP has a higher (more negative) conduction band

(CB) and Fermi level, while OP has a lower (more positive) valence band (VB). An advanced configuration uses internal electric fields and staggered band alignments to significantly enhance charge separation, often used with Bi_2WO_6 and BiOX .

Recent works have shown that bismuth-based S-scheme heterostructures have a high level of photocatalytic activity under visible light by facilitating a high rate of charge separation while maintaining a high redox potential (Ma et al., 2025; Tian et al., 2025). For example, bismuth oxybromide/titanium dioxide ($\text{BiOBr}/\text{TiO}_2$) S-scheme heterojunctions exhibited improved separation of photogenerated carriers and improved visible-light photocatalytic action because of close interfacial contact between the two constituents (Shkir and Ali, 2025). An iron(II, III) oxide/bismuth tungstate ($\text{Fe}_3\text{O}_4/\text{Bi}_2\text{WO}_6$) S-scheme heterojunction exhibited highly improved photocatalytic efficiency in the visible-light photodegradation of ciprofloxacin because of its outstanding interfacial charge transfer ability and enhanced separation of photogenerated carriers (Zhu et al., 2021). Other examples are bismuth molybdate/graphitic carbon nitride ($\text{Bi}_2\text{MoO}_6/\text{g-C}_3\text{N}_4$) (Le et al., 2025; Li et al., 2024a), Bi_2WO_6 /nickel oxide (NiO) (Li et al., 2023), tungsten trioxide (WO_3)/ BiOBr (Liu et al., 2022a), and bismuth vanadate/bismuth oxy-sulfide ($\text{BiVO}_4/\text{Bi}_2\text{O}_2\text{S}$) (Chen et al., 2025a). More complicated architectures like $\text{BiVO}_4/\text{g-C}_3\text{N}_4$ (Chen et al., 2022) S-scheme heterojunctions

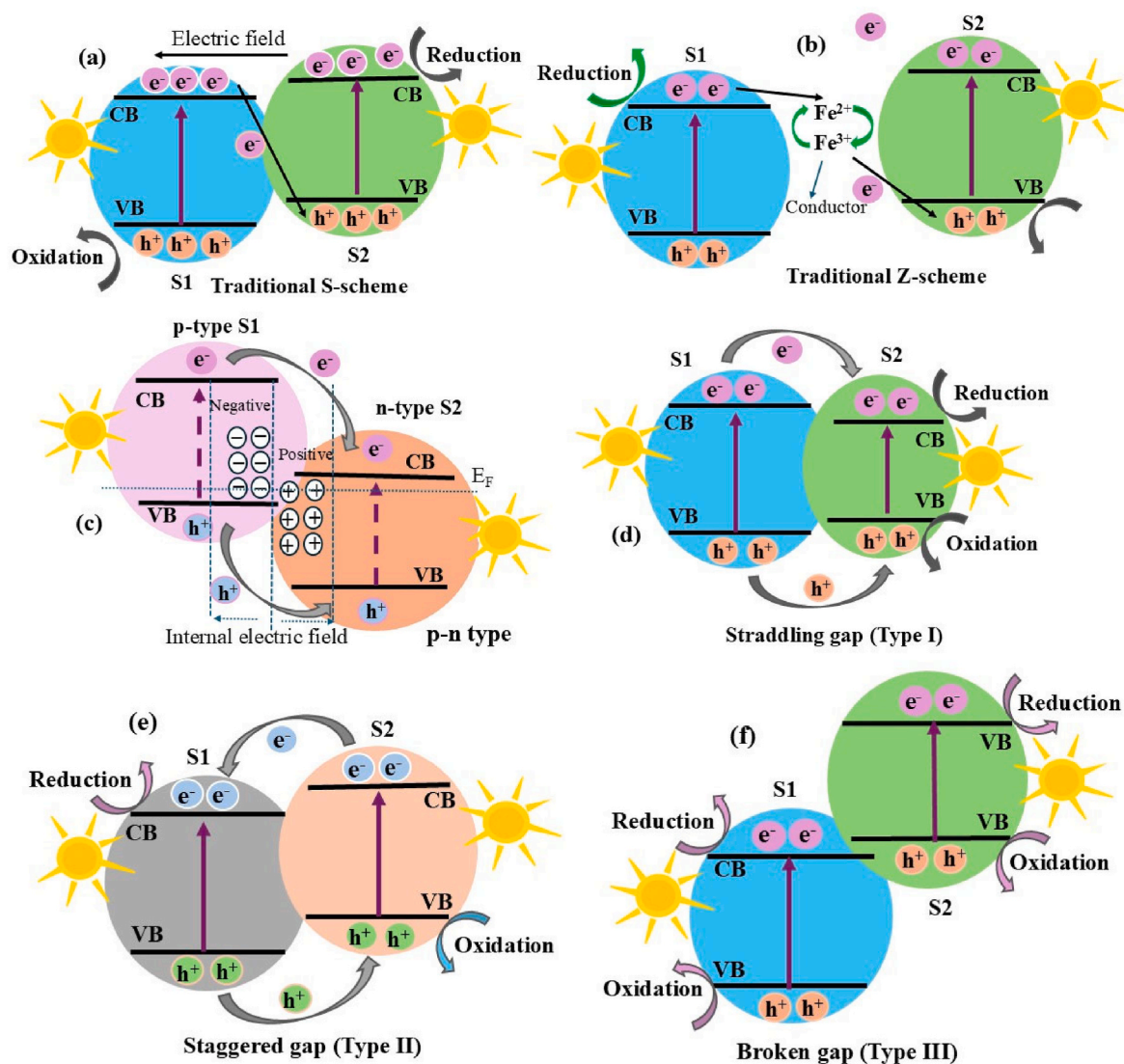


Fig. 1. Charge transfer and separation mechanism of electron and hole pairs in various types of heterojunction photocatalysts. (a) S-scheme, (b) Z-scheme, (c) p-n junction, (d) Type I, (e) Type II, and (f) Type III.

have already been suggested in order to achieve greater charge separation efficiency and expansion of visible-light absorption. Moreover, ternary or bilayer S-scheme, e.g., fluorine-doped-BiVO₄ (F-BiVO₄)/g-C₃N₄/cadmium sulfide (CdS) material, has also been reported to further augment photocatalytic effectiveness by utilizing synergistic charge transfer mechanisms (Yang et al., 2024). A ternary S-scheme like g-C₃N₄/BiOBr/Bi₂MoO₆ complexes were designed, which offered better photodegradation performance when applied to the photocatalysis of CIP, as such a type of heterojunction permits high absorption of light and directional charge transfer routes (Chankhanittha et al., 2024). Such types of heterojunctions were also applied in photocatalysis in the presence of other strong oxidants. The above discussion clearly shows that the design of the bismuth-based S-scheme heterojunction photocatalysts is an efficient method to retain strong oxidative holes and reductive electrons at the same time to enable effective production of reactive oxygen species, including superoxide anion ($\bullet\text{O}_2^-$) and hydroxyl ($\bullet\text{OH}$) radicals, which is important in the photodegradation of antibiotics, such as CIP and LEV.

2.2.2. Z-scheme

Like S-scheme heterojunctions, Z-schemes are also advanced photocatalytic configurations designed to overcome the limitations of conventional Type-II heterojunctions by suppressing the recombination of photogenerated electron-hole pairs while maximizing their redox potential. In a standard Z-scheme system based on natural photosynthesis, the primary mechanism is the two-stage, double-excitation process that enables the splitting of water into oxygen and hydrogen using visible light. The photogenerated electrons in the CB of one semiconductor react with the holes in the VB of another semiconductor via a redox mediator, a solid conductor, or direct contact. This recombination route enables the charge carriers that remain, i.e., the electrons in the CB of the reduction photocatalyst and the holes in the VB of the photocatalyst, to maintain potent reduction and oxidation capacities, which enhances photocatalytic performance. Nevertheless, the conventional model of the Z-scheme is predominantly used to characterize the charge transfer pathway, without a comprehensive description of the interfacial electronic structure and driving forces. Z-scheme photocatalysis mimics natural photosynthesis to efficiently separate photogenerated electrons and holes by arranging two different semiconductors (PC_I) and (PC_{II}) in a staggered band structure, creating a Z-shaped, 'downhill' energy transfer path (Li et al., 2022a). They efficiently separate photogenerated electrons and holes via a Z-shaped transfer pathway, overcoming the limitations of low efficiency and poor redox ability in conventional Type-II heterojunctions. In a Z-scheme photocatalytic system, electrons from the conduction band (CB) of the oxidation photocatalyst combine with holes from the valence band (VB) of the reduction photocatalyst, which preserves the most powerful redox charges (Nasir et al., 2021), as shown in Fig. 1b. Traditional Z-scheme heterojunctions use either liquid-phase reversible redox pairs (e.g., $\text{Fe}^{3+}/\text{Fe}^{2+}$, IO_3^-/I^- , $\text{NO}_3^-/\text{NO}_2^-$) or all-solid-state conductive materials (e.g., Au, Ag) as electron mediators to shuttle electrons between the two semiconductors to transfer charges between them. Examples are Ag/AgBr/BiVO₄ (Chen et al., 2018a), CdSe/Se/BiOBr (Du et al., 2022b), and BiOX/Bi₂MoO₆/Bi₂O₃ (Naeem et al., 2025). The newer generation dual Z-scheme heterojunctions are advanced multi-semiconductor photocatalytic systems designed to improve solar-to-chemical energy conversion by keeping photogenerated electrons and holes efficiently separated while maintaining high redox (reduction-oxidation) capabilities (Sun et al., 2025a). They have several advantages over traditional Z-scheme heterojunctions, such as prolonged charge carrier lifetime, enhanced solar light absorption, higher charge concentration, and superior redox capability (Liao et al., 2022). A few examples are bismuth oxychloride (BiOCl)/Bi₂MoO₆/CdS (Jiang et al., 2022), g-C₃N₄/BiVO₄/copper ferrate (CuFe₂O₄) (Li et al., 2023), Bi₂MoO₆/graphene quantum dots (GQDs)/TiO₂ (Lu et al., 2022), bismuth oxyiodide (BiOI)/BiVO₄/g-C₃N₄ (Zhu et al., 2022a), and silver phosphate (Ag₃PO₄)/g-C₃N₄/Bi₂WO₆

(Rhaya et al., 2025). Moreover, another Z-scheme heterojunction photocatalyst, zinc ferrite (ZnFe₂O₄)/BiVO₄, showed rapid degradation of CIP under visible light, and the degradation efficiency reached up to 97% due to the effective separation of electrons and holes and an increase in the formation of reactive oxygen species (Wang et al., 2023a). These investigations are a clear indication that the bismuth-based Z-scheme heterojunction photocatalysts have a high potential in the elimination of fluoroquinolone-based antibiotics in aqueous conditions, as they not only enhance visible light absorption but also inhibit recombination of charges and have strong oxidation and reduction properties, which are required to effectively degrade pollutants (Wang et al., 2023b).

The key difference between Z-scheme and S-scheme (step-scheme) heterojunctions lies in their internal charge transfer mechanisms. In S-scheme heterojunctions, a reduction photocatalyst (higher Fermi level) and an oxidation photocatalyst (lower Fermi level) are in direct contact, and when they join, Fermi level alignment creates an internal electric field and band bending at the interface. This built-in electric field combined with Coulombic attraction actively drives the recombination of useless, low-energy electrons and holes, leaving high-energy charge carriers trapped in their respective band. On the other hand, Z-scheme heterojunctions require an external or shuttle redox mediator to bridge the semiconductors to move electrons from the valence band of one semiconductor to the conduction band of the other.

2.2.3. p-n

A p-n type heterojunction is an interface between two physically or chemically different semiconductor materials, where one acts as a p-type (hole-dominant) semiconductor and the other acts as an n-type (electron-dominant) semiconductor. In a p-n junction, electrons and holes flow in opposite directions to create current (Fig. 1c). Electrons are negatively charged and flow from the n-type (negative) to the p-type (positive) region. Holes, which act as positive charge carriers (vacant spaces left by electrons), flow from the p-type to the n-type region. When a p-type semiconductor and an n-type semiconductor come into contact, their Fermi levels (E_F) must align at thermodynamic equilibrium. This causes a migration of charge carriers across the interface, creating a built-in electric field and a depletion region. For example, a bismuth-based BiOBr/g-C₃N₄ p-n type heterojunction is formed by connecting p-type BiOBr and n-type g-C₃N₄ to create internal electric fields that accelerate electron-hole separation. A traditional p-n heterojunction suffers from severe loss of redox potential and poor spatial charge separation compared to advanced S-scheme or Z-scheme photocatalysts. P-n heterojunction photocatalysts offer superior charge separation and higher degradation efficiency for organic pollutants compared to older-generation heterojunctions (e.g., Type II) due to a powerful internal built-in electric field (Che et al., 2023).

2.2.4. Type II

Type II heterojunctions are engineered interfaces between two semiconductors with staggered band alignment, where the conduction bands (CBs) and valence bands (VBs) of one material are higher than those of the other. This configuration enables spatial separation of photoexcited charge carriers; electrons accumulate in the lower conduction band and holes in the higher valence band, improving charge separation efficiency in photocatalysis. Semiconductor A has a higher CB and a higher VB compared to Semiconductor B. Upon illumination, electrons from the higher-energy CB transfer to the lower-energy CB, while holes move to the higher-energy VB. This spatial separation reduces charge recombination rates, enhancing efficiency. A staggered band alignment where electrons and holes migrate in opposite directions, as in systems like vanadium pentoxide (V₂O₅)/BiVO₄ (Balapure et al., 2024) and BiVO₄/TiO₂ (Peng et al., 2024). While separating carriers, the charge transfer mechanism often leads to a reduced redox potential compared to individual materials, as electrons move to a lower-potential CB and holes to a lower-potential VB, which is a

limitation.

Type-II heterojunctions have been broadly explored in bismuth systems of photocatalysts to degrade fluoroquinolone antibiotics. The CB and VB of the two semiconductors in a typical Type-II heterostructure are placed at elevated energy levels relative to the other semiconductor, favoring the movement of photogenerated electrons and holes in opposite directions (Fig. 1e). This geometrical segregation of charge carriers is an effective way of inhibiting electron-hole recombination and promoting photocatalytic reactions when they are irradiated by visible light (Cai et al., 2022). Several bismuth-based Type-II heterojunction photocatalysts were successfully studied for the photo-degradation of antibiotics. For example, a bismuth-doped indium-based metal-organic framework (MIL-68(In, Bi)-NH₂)/BiOBr heterojunction photocatalyst can be used to degrade CIP more effectively than other photocatalysts because of its wider-spectrum light absorption capacity (Zhang et al., 2022). Likewise, Type-II heterostructures of N-rich g-C₃N₅/Bi₄O₅Br₂ (bismuth oxybromide) are effective for the removal of antibiotics under visible light, with staggered and ideal band alignment to allow electron and hole flow through the two semiconductors (Tu et al., 2024). Although they exhibit better charge separation than Type I, they suffer from Coulombic repulsion and a reduced redox potential because electrons and holes accumulate on the weaker reducing/oxidizing sites.

2.2.5. Schottky junctions

Schottky heterojunctions are specialized metal-semiconductor interfaces that form a rectifying barrier, typically when a metal with a high work function contacts an n-type semiconductor. They are characterized by low turn-on voltage (0.2–0.3 V), high-speed switching, and majority carrier transport, making them ideal for diodes and photocatalysts. A Schottky junction is created when the metal work function (ϕ_m) is greater than the semiconductor work function (ϕ_s). The difference in Fermi levels creates a potential barrier at the interface, causing band bending in the semiconductor and forming a depletion region. Metal-semiconductor contacts, such as Ag/BiOBr, improve charge carrier separation at the interface. Yan et al. reported the synthesis of a Schottky junction photocatalyst with a Bi/Bi₂O₃ core-shell nanoparticle modified with g-C₃N₄, which considerably improves the separation and transfer efficiency of photogenerated electron-hole pairs (Yan et al., 2023).

2.2.6. Type I and type III

Type I and Type III heterojunctions are semiconductor interfaces defined by distinct energy band alignments and are less common, involving straddling or broken band alignments, respectively. Type I (straddling gap) features one material's bandgap entirely inside the other's, ideal for LEDs and lasers. In Type-I (straddling gap) heterojunctions, the bandgap of one semiconductor sits completely inside the larger bandgap of the second. Because of this alignment, both photogenerated electrons and holes naturally migrate toward and accumulate within the same narrower-bandgap material, making it an ideal setup for confining charge carriers in lasers but highly inefficient for photocatalysis. In the case of Type I, the CB of Material A is lower, and its VB is higher than those of Material B (Fig. 1d) (Kistner-Morris et al., 2024). The smaller bandgap (E_{g1}) is completely straddled by the larger bandgap (E_{g2}). Electrons and holes both accumulate in the material with the smaller bandgap (Material A). Type I heterojunctions, such as gallium arsenide/aluminum gallium arsenide (GaAs/AlGaAs), CdS/ZnS, and TiO₂/ZnS, are primarily used for light-emitting diodes (LEDs) and lasers because of the strong confinement of electrons and holes in the same region, enhancing recombination (Yu et al., 2025). Poor charge separation efficiency because carriers accumulate on a single component, leading to high recombination rates. They generally show lower degradation activity than Type-II.

Type III (broken gap) has completely staggered bands where the valence band of one lies above the conduction band of the other, enabling unique charge transfer and potential for specialized electronics

(Fig. 1f. In the case of Type III heterojunctions, the bands are heavily staggered to the point of breaking. The valence band of one material lies above the conduction band of the other. No overlap between the forbidden gaps of the two materials occurs, creating a "broken" gap structure, which allows unconventional separation of charge carriers. Type III can lead to extreme band alignment scenarios with unique charge transfer mechanisms, often studied in organic electronics (Qiao et al., 2022). Potential for advanced, high-speed electron-hole tunneling devices, specialized photo-detectors, and specific optoelectronic applications. Common examples are gallium antimonide/indium arsenide (GaSb/InAs), indium arsenide/aluminum antimonide (InAs/AlSb), gallium oxide/silicon carbide (Ga₂O₃/SiC), and oxygen-deficient tungsten trioxide/gadolinium orthochromate (WO_{3-x}/GdCrO₃), and they are used primarily in advanced high-speed electronic, tunneling, and optoelectronic semiconductor devices. Type III heterojunctions are not used in the photocatalysis of pollutants because their band gaps do not overlap (broken-gap alignment), which prevents the effective migration and spatial separation of photogenerated electron-hole pairs (Guo et al., 2024).

3. Synthesis of heterojunction photocatalysts

Popular synthesis processes include hydrothermal, solvothermal, sol-gel, precipitation, co-precipitation, and ultrasonication. Initial studies used hydrothermal and solvothermal methods to synthesize heterojunction photocatalysts, and they are still the two most studied synthesis methods. In the hydrothermal method, the reactants are dissolved in water, the solution is placed in a high-pressure vessel (autoclave), and heated at 150 to 200 °C under high pressure, producing highly crystalline structures. Chai et al. first reported the synthesis of a bismuth-based heterojunction photocatalyst, BiOCl/Bi₂O₃, by the hydrothermal method to overcome the issues of other heterojunction photocatalysts (Chai et al., 2009). The solvothermal method is similar to the hydrothermal method except that the reactants are dissolved in a solvent instead of water. The two processes are schematically illustrated in Fig. 2. The sol-gel method forms heterojunctions by converting liquid photocatalyst precursors into an interconnected solid network via hydrolysis and condensation, allowing for precise control of band alignments and intimate interfacial contact between two different semiconductors. For example, Liu et al. reported the synthesis of a Z-scheme Bi₂O₃/CuBi₂O₄ (copper bismuth oxide) heterojunction by the sol-gel method (Liu et al., 2023a). Precipitation is a facile, bottom-up method for forming semiconductor heterojunctions by reacting dissolved bismuth-based precursors to deposit a secondary phase onto a primary material, producing high-purity, structurally robust interfaces that suppress charge recombination. For example, Lai et al. reported the synthesis of a CuS (copper sulfide)/BiVO₄ heterojunction by the precipitation method (Lai et al., 2019). Jia et al. reported the synthesis of a CuFe₂O₄/Bi₂MoO₆ heterojunction by precipitation followed by the hydrothermal method (Jia et al., 2024). The co-precipitation method is similar to the precipitation method except that multiple precursors are precipitated together in a single solution by adding a precipitating agent to co-deposit them simultaneously. For example, Abou Taleb et al. reported the synthesis of a BiVO₄/Bi₂S₃ (bismuth (III) sulfide) Z-scheme heterojunction by the co-precipitation method (2023Abou Taleb et al., 2023).

Based on the heterojunction formation mechanisms, the synthesis methods can be divided into electrostatic self-assembly, ion-exchange, and in-situ growth. An in-situ growth method for bismuth-based heterojunctions involves directly synthesizing secondary bismuth material on or within an existing substrate or precursor, creating seamless atomic-level contact and improving charge transfer. For example, Xie et al. reported the synthesis of α -Fe₂O₃ (ferric oxide)/Bi₂WO₆ layered heterojunctions by an *in-situ* growth strategy (Xie et al., 2019). Initially, Bi₂WO₆ was formed by the hydrothermal method, and then α -Fe₂O₃ was grown and deposited on the surface of Bi₂WO₆. In the case of the

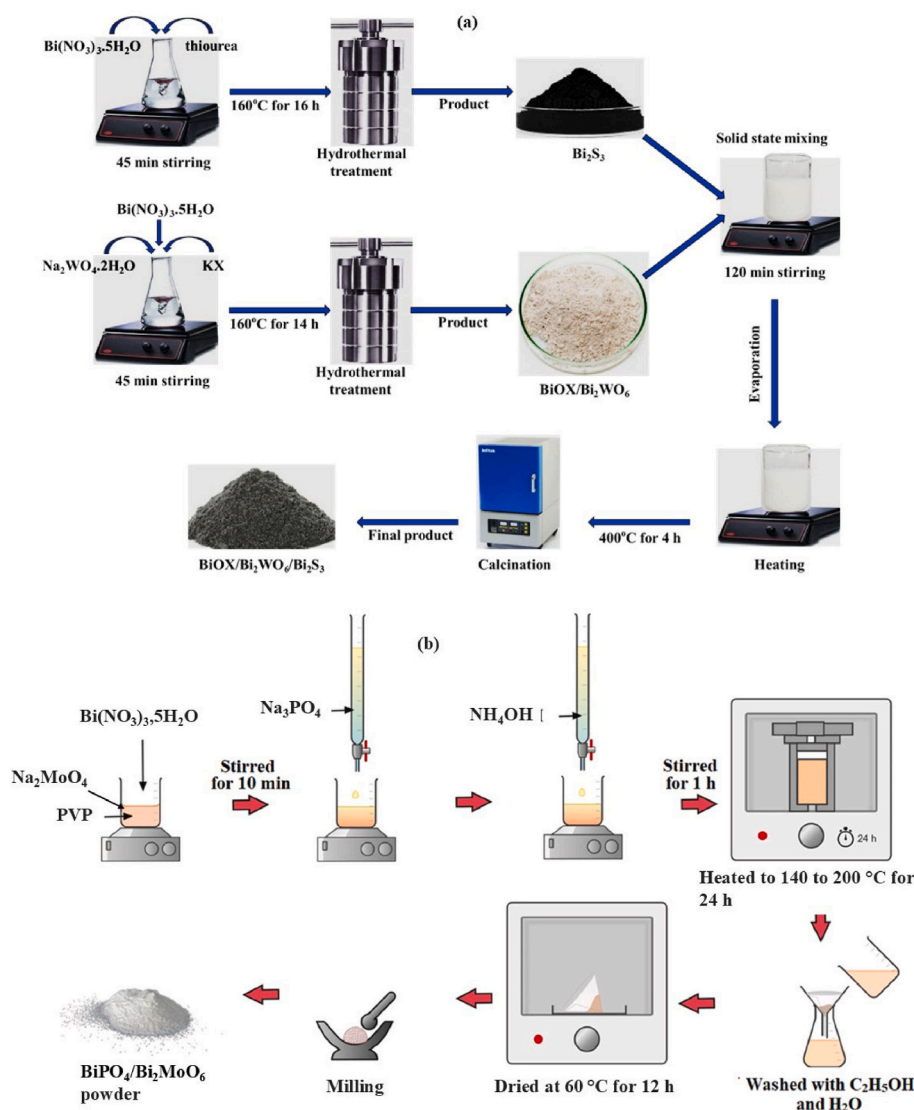


Fig. 2. Schematic diagram of (a) hydrothermal synthesis of BiOX/Bi₂WO₆/Bi₂S₃ and (b) solvothermal synthesis of bismuth phosphate (BiPO₄)/Bi₂MoO₆ heterojunctions.

formation of a heterojunction by electrostatic self-assembly, two pre-existing photocatalysts with opposite electrical charges are mixed so they attract and stick together to form a layered heterojunction structure. For example, Feng et al. reported the synthesis of a 1D/2D WO₃/BiOBr_{0.5}Cl_{0.5} (bismuth oxybromochloride) heterojunction photocatalyst via the electrostatic self-assembly method from hydrothermally prepared WO₃ nanorods having a zeta potential of −39.8 mV and BiOBr_{0.5}Cl_{0.5} prepared by the precipitation method having a zeta potential of 13.8 MV (Feng et al., 2023). The synthesis of bismuth stannate/β-bismuth trioxide (Bi₂Sn₂O₇)/β-Bi₂O₃ S-scheme heterojunction by the electrostatic self-assembly method was also reported (Zhu et al., 2023). The ion-exchange method is a wet-chemical, top-down method that is used to synthesize or modify heterojunctions. It involves substitution of specific ions in a pre-synthesized parent crystal (like cations or anions) with others from a surrounding solution, forcing a phase transition that inherently constructs a tight, defect-free junction between the newly formed phase and the unreacted core. For example, Xie et al. reported the synthesis of a silver bromide (AgBr)/BiOBr S-scheme heterojunction using an ion exchange strategy (Xing et al., 2022).

4. Photodegradation of CIP and LEV

4.1. Photodegradation performance of CIP

Table 1 summarizes the photocatalytic degradation performance of different bismuth-based heterojunction photocatalysts, which have been reported to remove CIP in water. In general, most of the systems reported have high degradation efficiencies when light of visible wavelengths is irradiated on them, suggesting that bismuth-based materials have a high potential for removing antibiotics in water under visible light, reducing the energy cost. Of the mentioned photocatalysts, the literature is dominated by Z-scheme heterojunction systems that are capable of maintaining strong redox potential and improving the separation of the charge carriers. It is difficult to make a true comparison of the photocatalytic performance of various heterojunctions for the destruction of LIV and CIP when their concentration, photocatalyst dose, pH, light source and light intensity, and degradation time are different in various published works. For example, the degradation of CIP by Fe₃O₄/Bi₂WO₆ S-scheme heterojunction reached a high degradation efficiency of 99.7% in a short 15-min photodegradation, which reflects the efficiency of magnetic bismuth tungstate systems as a way of removing antibiotics. Equally, the CdSe/Se/BiOBr and ZnFe₂O₄/BiVO₄ Z-scheme

Table 1

Performance of bismuth-based heterojunctions for the photodegradation of CIP.

Photocatalysts	Method	Type	Reaction conditions					Degradation efficiency (%)	Rate constant (min ⁻¹)	Kinetic model	Ref.
			Drug conc. (mg/L)	Catalyst loading (g/L)	Treatment time (min)	pH	Light source				
BiVO ₄ -Bi ₂ S ₃ /MXene	Solvothermal	Type II	n/a	n/a	70	n/a	400 W Tungsten	37.0	0.007	PFO	Abou Taleb et al. (2023)
g-C ₃ N ₄ /BiOBr/Bi ₂ MoO ₆	Solvothermal	S-scheme	10	0.05	60	3	15 W LED	92.0	0.014	FO	Chankhanittha et al. (2024)
Fe ₃ O ₄ /Bi ₂ WO ₆	Hydrothermal	S-scheme	10	0.3	15	n/a	500 W Xe	99.7	0.5571	PFO	Zhu et al. (2021)
ZnFe ₂ O ₄ /BiVO ₄	Solvothermal	Z-scheme	20	n/a	30	n/a	Visible	97.0	n/a	n/a	Wang et al. (2023a)
Bi ₂ Sn ₂ O ₇ /SnS ₂	Hydrothermal	S-scheme	10	0.15	120	n/a	300 W Xe	85.0	0.0178	PFO	Ji et al. (2026)
Bi ₂ WO ₆ /BiO _{2-x}	Hydrothermal	Z-scheme	10	0.5	120	3.0	300 W Xe	91.8	n/a		Zhang et al. (2023a)
Bi ₅ O ₇ I/Uio-66-NH ₂	Solvothermal	S-scheme	10	0.75	120	7.8	300 W Xe	96.1	0.0136	PFO	Zhao et al. (2021)
BiOCl/Bi ₂ WO ₆ /Bi ₂ S ₃	Hydrothermal	S-scheme	5	0.6	120	9.0	200 W Tungsten	96.6	0.023	PFO	Naeem et al. (2026a)
Ag/AgBr/BiVO ₄	Hydrothermal	Z-scheme	10	n/a	60	6.5	300 W Xe	91.4	0.0192	LHFO	Chen et al. (2018a)
MIL-88B(Fe)/BiOBr with H ₂ O ₂	Solvothermal	Z-scheme	10	0.2	90	5.7	300 W Xe	94.6	0.0227	QFO	Liu et al. (2024a)
Cd-doped Ag ₂ O/BiVO ₄	Hydrothermal	Z-scheme	10	n/a	60	3.0	14 W LED	75.0	0.009	PFO	De et al. (2022)
CDs/Bi ₄ O ₅ Br ₂	Solvothermal	S-scheme	10	0.2	120	n/a	500 W Xe	98.0	0.0313	PFO	Zhang et al. (2019)
g-C ₃ N ₄ /Bi ₄ O ₅ Br ₂	Thermal exfoliation	S-scheme	10	0.5	75	n/a	300 W Xe	90.0	n/a	n/a	Ji et al. (2017)
Fe ₃ O ₄ /Bi ₂ WO ₆	Solvothermal	S-scheme	15	1.0	120	n/a	300 W Xe	90.0	0.008	FO	Song et al. (2020)
g-C ₃ N ₄ /Bi ₂ WO ₆	Solvothermal	S-scheme	15	1.0	120	n/a	300 W Xe	98.0	n/a	n/a	Mao et al. (2019)
Bi ₁₂ O ₁₇ Cl ₂ /Uio-66-NH ₂	Solvothermal	Z-scheme	10	0.5	60	7.0	300 W Xe	83.5	0.0307	FO	Chu et al. (2024)
Ag ₃ PO ₄ /g-C ₃ N ₄ /Bi ₂ WO ₆	Hydrothermal	Dual Z-scheme	20	1.0	90	7.0	Solar light	94.0	0.0214	PFO	Rhaya et al. (2025)
MgIn ₂ S ₄ /BiOBr	Hydrothermal	S-scheme	10	0.8	60	7.0	100 W Xe	89.9	0.031	PFO	Yusuf et al. (2026)
H-C ₃ N ₄ /FeNi ₂ S ₄	Solvothermal	S-scheme	10	0.7	100	6.0	300 W Xe	95.2	0.017	PFO	Rana et al. (2025)
Fe ₂ O ₃ /BiOI@BiOBr	Solvothermal	Z-scheme	10	n/a	60	5.5	UV-C	92.0	0.037	PFO	Feitosa et al. (2024)
Bi ₂ MoO ₆ /GQDs/TiO ₂	Hydrothermal	Z-scheme	10	n/a	150	n/a	300 W Xe	90.2	0.0155	FO	Lu et al. (2022)
g-C ₃ N ₄ /ZnO	Hydrothermal	S-scheme	10	n/a	180	n/a	Sunlight	96.0	n/a	n/a	Gayathri et al. (2022)
CdSe/Se/BiOBr	Solvothermal	Z-scheme	20	1.0	240	n/a	300 W Xe	97.5	0.1124	PFO	Du et al., (2022a)
BiOBr/TiO ₂	Hydrothermal	S-scheme	n/a	0.2	120	n/a	300 W MH	93.0	0.0226	PFO	Shkir and Ali (2025)
WS ₂ /Bi ₂ MoO ₆	Hydrothermal	S-scheme	10	1.0	180	8.0	500 W Xe	98.9	0.0367	FO	Li et al. (2018)
Bi ₂ WO ₆ /Bi ₃ O ₄ Cl	Hydrothermal	S-scheme	10	0.15	90	7.0	300 W Xe	92.5	0.02373	PFO	Zhang et al. (2026a)
BiOBr/Bi ₂ MoO ₆	Hydrothermal	S-scheme	10	1.0	120	n/a	300 W Xe	84.6	0.37613	FO	Wang et al. (2017)
BiFeO ₃ /BiVO ₄	Hydrothermal	p-n	5	n/a	240	6.8	100 W Xe	80.3	0.0062	PFO	Nkwachukwu et al. (2023)
BiOBr/BiFeO ₃	Hydrothermal	S-scheme	5	0.02	120	n/a	500W + sonication	76.5	0.023	FO	Liu et al. (2022b)
Bi/BiOBr	Solid-state mixing	p-n	20	0.1	60	n/a	25 W FL	94.8	0.029	PFO	Imam et al. (2019)
Ag/Ag ₆ Si ₂ O ₇ /Bi ₂ MoO ₆	Hydrothermal	p-n	20	0.5	120	n/a	300 W Xe	96.6	0.0141	PFO	Li et al. (2021a)
Bi ₂ O ₃ /(BiO) ₂ CO ₃	Hydrothermal	p-n	10	0.5	30	4-8	300 W Xe	93.4	0.476	PFO	Chen et al. (2018b)
BiOX/Bi ₂ MoO ₆ /Bi ₂ S ₃ (X = Cl, Br, I)	Hydrothermal	Z-scheme	10	0.2-1.0	120	3-11	200 W T	94.0	0.019	PFO	Naeem et al. (2026b)
BiOX/Bi ₂ MoO ₆ /Bi ₂ O ₃ (X = Cl, Br, I)	Hydrothermal	Z-scheme	5	0.5	120	7-8	200 W T	90.7	0.017	PFO	Naeem et al. (2025)

(continued on next page)

Table 1 (continued)

Photocatalysts	Method	Type	Reaction conditions					Degradation efficiency (%)	Rate constant (min ⁻¹)	Kinetic model	Ref.
			Drug conc. (mg/L)	Catalyst loading (g/L)	Treatment time (min)	pH	Light source				
Bi ₂ MoO ₆ /CuBi ₂ O ₄	Hydrothermal	S-scheme	10	1.0	180	n/a	500 W Xe	90.2	n/a	PFO	Li et al. (2021b)
Bi ₂ MoO ₆ /Sr ₂ Nb ₂ O ₇	Hydrothermal	Type I	10	0.3	90	12	300 W Xe	96.3	0.014	PFO	Alduhaish et al. (2025)
Bi ₂ WO ₆ /BiOI	Hydrothermal	S-scheme	20	1.0	80	10	300 W Xe	76.7	0.0155	PFO	Zou et al. (2022)
Bi-Bi ₂ WO ₆ /BiOI		Z-scheme						96.0	0.0335		
Bi ₂ MoO ₆ /g-C ₃ N ₄ /BiFeO ₃	Solvothermal	Z-scheme	12	0.1	180		500 W Xe	95.0	0.014	PFO	Zhou et al. (2022)
CQDs/Bi ₂ MoO ₆	Hydrothermal	S-scheme	20	0.05	180	3-11	300 W Xe	97.7	0.009	PFO	Liu et al. (2025b)
Bi ₂ MoO ₆ /g-C ₃ N ₄	Solvothermal	S-Scheme	10	0.04	90	3-7	Visible light	94.0	0.02464	PFO	Fan et al. (2025)
Bi ₂ MoO ₆ /Bi ₄ Ti ₃ O ₁₂	Solvothermal	Z-scheme	10	0.5	120	9	300 W T	90.0	0.015	FO	Bharathi et al. (2025)
Bi ₂ MoO ₆ /g-C ₃ N ₄	Hydrothermal	S-scheme	50	0.05	120	n/a	Visible light	55.3	0.0126	PFO	Li et al. (2020)
KBCN/t-BiVO ₄ /m-BiVO ₄	Hydrothermal	S-scheme	10	0.04	60	5-9	300 W Xe	93.0	0.0124	PFO	Chen et al. (2024b)
SnS ₂ /Bi ₂ MoO ₆	Hydrothermal	Z-scheme	10	n/a	120	n/a	5 W LED	90.0	n/a	n/a	Liu et al. (2018)
CdS/Bi ₂ MoO ₆ /RGO	Hydrothermal	Z-scheme	20	5.0	60	n/a	300 W Xe	91.0	n/a	n/a	Chen et al. (2020)
BiVO ₄ /Bi ₂ S ₃	Co-precipitation	Z-scheme	7	0.03	70	n/a	400 W T	71.3	0.016	PFO	Abou Taleb et al. (2023)
BiPO ₄ /Bi ₂ WO ₆	Solvothermal	Z-scheme	20		120	n/a	300 W Xe	94.5	n/a	n/a	Zhang et al. (2026b)
Bi ₂ MoO ₆ /rGO	Hydrothermal	S-scheme	20	1.0	360	n/a	300 W Xe	90.0	n/a	n/a	Bai et al. (2017)
Bi ₂ WO ₆ /PANI	Hydrothermal	p-n	10	0.5	90	n/a	Sunlight	98.0	0.0411	PFO	Tahir et al. (2020)
N-CD/Bi ₂ MoO ₆ /g-C ₃ N ₄	Hydrothermal	Z-scheme	3	1.0	30	n/a	300 W Xe	99.0	0.13	PFO	Dang et al. (2021)
Bi ₂ S ₃ /Bi ₂ O ₃	Hydrothermal	S-scheme	12	1	110	10	40 W Hg	33	0.099	PFO	Bahmani et al. (2025)
Cu ₃ SnS ₄ /L-BiOBr	Hydrothermal	S-scheme	10	0.05	180	n/a	300 W Xe	93	n/a	PFO	Li et al. (2022b)
Ag-Bi ₂ O ₃ /CdS	Hydrothermal	S-Scheme	20	0.03	60	7	Sunlight	93	0.0291	FO	Chakinala and Gogate (2025)
CuS/BiVO ₄	Precipitation	p-n	10	0.1	90	n/a	300 W Xe	86.7	0.021	FO	Lai et al. (2019)
Bi ₂ S ₃ /BiOCl	Precipitation	S-scheme	10	0.03	180	n/a	500 W MH	71.2	n/a	n/a	Liu et al. (2021)
Bi ₂ O ₂ S/Bi ₂ O ₃	Precipitation	S-scheme	20	0.05	6	n/a	300 W Xe	91		n/a	Zheng et al. (2025)
BiOCl/Cu-Bi ₂ S ₃	Hydrothermal	Z-scheme	20	0.02	20	n/a	300 W Xe	97.1	0.1119	PFO	Du et al., (2022b)

N.B.: Xe = Xenon bulb, T = Tungsten bulb, LED = light-emitting diode bulb, FL = Fluorescent bulb, and MH = Metal halogen bulb, CDs = carbon dots, MIL-88B(Fe) = iron-based metal-organic framework, MWCNT = multi-walled carbon nanotube, rGO = reduced graphene oxide, KBCN = potassium bromide-modified graphitic carbon nitride, PANI = polyaniline, N-CD = nitrogen-doped carbon dots, Cu-Bi₂S₃ copper-doped bismuth sulfide.

photocatalysts had high photocatalytic characteristics with degradation efficiencies of 97.0 and 97.5%, respectively, under visible light. Besides, Bi₂MoO₆-based Z-scheme composites, including Bi₂MoO₆/Bi₄Ti₃O₁₂ (bismuth titanate, Bi₂MoO₆/GQDs/TiO₂, and g-C₃N₄/Bi₂MoO₆, have been shown to have high photocatalytic potential with comparable degradation efficiencies of around 90% due to enhanced interfacial charge transfer and visible-light absorption.

S-scheme heterojunction systems have also been reported at an increasing rate because of their capability to hold very reductive electrons and strongly oxidative holes at the same time. As an illustration, the S-scheme photocatalysts of BiOCl/Bi₂WO₆/Bi₂S₃ could be used to achieve 96.6% degradation efficiency in 120 min, whereas the S-scheme photocatalysts of carbon quantum dots-modified Bi₂MoO₆ were able to achieve 97.7% removal efficiency. Equally, systems based on Cu₃SnS₄/L-BiOBr (lanthanum-doped BiOBr) and Bi₂O₂S/Bi₂O₃ S-schemes showed degradation efficiencies of about 93–91% that S-scheme structures are

viable in improving photocatalytic efficiency by way of improved charge separation and maintenance of strong redox capacity.

A few ternary and dual Z-systems have also been invented to further enhance photocatalytic efficiency. As an illustration, the Ag₃PO₄/g-C₃N₄/Bi₂WO₆ dual Z-scheme photocatalyst reached 94% degradation with solar light, showing the benefit of multi-component systems to promote directional charge transfer and broaden light absorption (Rhaya et al., 2025). Similarly, BiOX/Bi₂MoO₆/Bi₂S₃ ternary heterostructures demonstrated degradation efficiencies as high as 96.6% with the three semiconductor elements interacting synergistically. Hybrid photocatalysts that are metal-modified and carbon-based have also recorded encouraging outcomes. To give an example, Bi₂WO₆/PANI composites were found to degrade by 98%, and carbon quantum dots/Bi₂MoO₆ and g-C₃N₄/Bi₄O₅Br₂ composites were found to be very effective in increasing photocatalytic activity since they promoted electron mobility and light collection. Graphene nanoplatelets (GNPs),

multi-walled carbon nanotubes (MWCNTs), and fullerene quantum dots can also be used as carbon-based materials added to bismuth-based photocatalysts to attain carbon-to-carbon charge transfer and to prevent recombination of photogenerated carriers. Although many heterojunction systems have better performance, certain single-component photocatalysts have relatively lower degradation efficiencies. For example, BiFeO₃ has 77% degradation under sunlight, and Bi₂S₃/Bi₂O₃ heterostructures have relatively low degradation (33%), which means that suitable band alignment and interfacial charge transfer are the keys to effective photocatalytic work. Moreover, it is found that Bi₂WO₆ and Bi₂MoO₆-based photocatalysts are some of the most popular materials for degrading antibiotics because they have the appropriate band structures, responsiveness to visible light, and can be easily prepared in heterojunctions. The information in Table 1 reveals that bismuth-based heterojunction photocatalysts, specifically Z-scheme and S-systems, are essential in increasing the efficiency of photocatalytic degradation of CIP.

4.2. Photodegradation performance of LEV

In Table 2, the photocatalytic degradation efficiency of different bismuth-based heterojunction photocatalysts has been listed for the removal of LEV. Like CIP degradation systems, most studies used an initial LEV concentration of 5–25 mg/L, a catalyst loading of 0.02–0.75 g/L, and the most common light source was xenon lamps, which could be used to mimic the effect of the sun, but compact fluorescent lamps, tungsten lamps, light-emitting diodes (LEDs), and natural sunlight were also used in a few studies. The findings illustrate that the heterojunction photocatalysts based on bismuth have a high level of photocatalytic removal of LEV as compared to single-component materials.

Z-scheme heterojunction photocatalysts are some of the most studied systems among the documented systems because they can maintain a strong redox potential as well as facilitate efficient charge separation. As an example, the g-C₃N₄/BiVO₄/CuFe₂O₄ Z-scheme heterojunction recorded a 96.2% degradation of LEV under a 300 W Xe lamp in the presence of peroxymonosulfuric acid (PMS). On the same note, BiVO₄/g-C₃N₄ in combination with PMS had a degradation efficiency of 97.7% in just 40 min, which showed that the combination of oxidants and photocatalytic systems can continue to improve the degradation activity. Even other Z-scheme systems, such as rGO/Bi₂WO₆, bismuth tantalate/manganese cadmium sulfide (Bi₃TaO₇/Mn_{0.5}Cd_{0.5}S), and Bi₂WO₆/CD (carbon dots)/TiO₂, showed high degradation efficiencies of more than 85–92%, showing the effectiveness of Z-scheme charge transfer routes in enhancing photocatalytic processes.

The heterojunction photocatalysts, S-scheme heterojunctions, have also gained growing popularity because they are capable of retaining highly oxidative holes and strongly reductive electrons at the same time. As an example, g-C₃N₄/Bi₂WO₆ S-scheme photocatalysts demonstrated high degradation capability with an efficiency of 98.1% under simulated sunlight. On the same note, S-schemes containing cadmium indium sulfide (CdIn₂S₄)/Bi₂MoO₆ S-scheme photocatalysts exhibited 93.7% degradation in 90 min, and cobalt(II, III) oxide (Co₃O₄)/Bi₂MoO₆ S-scheme photocatalysts contained in g-C₃N₄ exhibited 95.2% degradation efficiency, indicating that multi-component heterostructures are beneficial in increasing charge separation and reactive oxygen species generation. Another interesting case is Bi₂MoO₆/molybdenum disulfide (MoS₂) S-scheme photocatalysts that had a degradation efficiency of 96.3% in just 25 min, which indicates that defect engineering and heterojunction assembly could greatly accelerate antibiotic degradation. Photocatalytic activity has also been seen to be enhanced by several ternary and carbon-modified photocatalysts. As an example, Bi₂O₃/CdBi₂O₄/BiOBr ternary Z-scheme systems were reported to exhibit 86.3 per cent degradation efficiencies under sunlight, whereas Bi₂WO₆/C-dots/TiO₂ Z-scheme heterostructures and Bi₂S₃@Zn-Co layered systems reported about 90% degradation efficiencies. The addition of conductive carbon materials, including reduced graphene oxide (rGO) or carbon

dots, has been found to allow the movement of electrons and inhibit the recombination of the photogenerated charge carriers, promoting photocatalytic efficiency.

Even though the performance of many heterojunction systems is tremendous, various single-component photocatalysts have relatively low degradation efficiencies. As an example, pristine BiVO₄ was able to degrade with about 76% degradation efficiency, with Bi₂WO₆ and Bi₄Ti₃O₁₂ having degradation efficiencies of 80 and 72.5%, respectively. All these findings indicate that the engineering of heterostructures is important in the enhancement of photocatalytic activity since it increases visible light absorption, efficient separation of charges, and the generation of reactive oxygen species, which cause the degradation of antibiotics. In general, the results reported in Table 2 suggest that bismuth-based heterojunction photocatalysts, especially Z- and S-schemes, have a high photocatalytic efficiency in LEV degradation.

4.3. Reaction kinetics

A range of models, such as zero-order (ZO), Langmuir-Hinshelwood first-order (LHFO), quasi-first-order (QFO), first-order (FO), pseudo-first-order (PFO), pseudo-second-order (PSO), Weber-Morris model, and liquid film diffusion model, have been utilized to describe and predict the sunlight-induced reaction kinetics and photodegradation rate of LEV and CIP by bismuth-based heterojunctions. Tables 1 and 2 show the kinetic models and reaction constants of photodegradation of LEV and CIP by various heterojunctions. It is evident that in most cases, the reaction rate followed the PFO and FO models, and in some cases, the L-H FO and QFO models. Therefore, we will limit our discussion only to these kinetic models. A first-order kinetic model describes the degradation of a reactant (e.g., pharmaceutical drugs) where the rate of reaction (degradation, or release) is directly proportional to the concentration of a single reactant, changing linearly with time. The linear equation of the first-order reaction is as follows:

$$\ln \left(\frac{C_t}{C_0} \right) = -k_t \quad [1]$$

where C_t and C_0 are the concentrations of the reactant at time t and 0, respectively, and k is the first-order rate constant. A plot of $\ln(C_t/C_0)$ versus t (min or s) yields a straight line with a slope of $-k$. The LHFO model was used for characterizing solid catalytic reactions, which consist of four steps: adsorption of reactant molecules on a catalytic surface, dissociation of adsorbed reactant molecules, reactions of dissociated reactant molecules to produce products, and desorption of products.

$$\frac{-t}{C_t - C_0} = \frac{1}{k_1} + \frac{1}{k_1 K} \frac{\ln \left(\frac{C_t}{C_0} \right) x^2}{C_t - C_0} \quad [2]$$

where C_t and C_0 are the concentrations of the reactant at time t and 0, respectively; K = adsorption rate constant/desorption rate constant, and k_1 is the degradation constant. Basha et al. carried out photocatalytic degradation of amoxicillin by the activated carbon-supported TiO₂ nanoparticles as integrated photocatalytic adsorbents (Basha et al., 2011). They found that the LHFO model exhibited a better fit than the first-order kinetics. The PFO kinetic model is widely used to describe photocatalytic degradation of various reactants when the reactant concentrations are low, often $<10^{-3}$ mol/L. The linear PFO equation is as follows:

$$\ln \left(\frac{C_0}{C_t} \right) = -k_t \quad [3]$$

where C_t and C_0 are the concentrations of the reactant at time t and 0, respectively, and k is the first-order rate constant. It simplifies the Langmuir-Hinshelwood kinetic model, assuming that the catalyst

Table 2

Photodegradation efficiency of LEV by various bismuth-based heterojunctions.

Photocatalysts	Type	Method	Reaction conditions					Degradation efficiency (%)	Rate constant (min ⁻¹)	Kinetic model	Ref.
			Drug conc. (mg/L)	Catalyst loading (g/L)	Treatment time (min)	pH	Light source				
BiVO ₄ /g-C ₃ N ₄	Hydrothermal	S-scheme	20	0.4	40	6.9	400 W Xe/PMS	97.7	n/a	PFO	Guo et al. (2025)
Bi ₂ WO ₆ /BiOI	Hydrothermal	S-scheme	20	1.0	60	10	300 W Xe	68.1	0.0129	PFO	Zou et al. (2022)
Bi-Bi ₂ WO ₆ /BiOI		Z-scheme						83.3	0.0206		
g-C ₃ N ₄ /BiVO ₄ /CuFe ₂ O ₄	Hydrothermal	Dual Z-scheme	10	0.2	60	n/a	300 W Xe/PMS	96.2	0.0542	PFO	Li et al. (2023)
Bi ₂ WO ₆ /TiO ₂ nanotube with PMS	Solvothermal	S-scheme	10		150	3-11	300W Xe	93.6	0.0171	PFO	Xia et al. (2026a)
Bi ₄ O ₅ Br/Bi ₅ O ₇ I _{0.7} Br _{0.3}	Hydrothermal	S-scheme	10	0.5	60	n/a	250 W Xe	88.4	0.0367	FO	Xia et al. (2026b)
g-C ₃ N ₄ /Bi ₂ WO ₆	Hydrothermal	S-scheme	15	n/a	180	n/a	Simulated sunlight	98.1	0.0443	PFO	Wei et al. (2025)
rGO/Bi ₂ WO ₆	Hydrothermal	Z-scheme	10	0.25	120	6.0	85 W FL	74.3	n/a	n/a	Arya et al. (2020)
Bi ⁰ /g-C ₃ N ₄ /Bi ₂ WO ₆	Solvothermal	S-scheme	20	0.5	120	n/a	300 W Xe	81.7	0.071	PFO	Lv et al. (2025)
Bi ₃ TaO ₇ /CdS	Hydrothermal	S-scheme	5	0.6	60	n/a	300 W Xe	76.5	0.0543	FO	Xu et al. (2020)
Bi ₃ TaO ₇ /Mn _{0.5} Cd _{0.5} S	Hydrothermal	S-scheme	5	0.6	60	n/a	300 W Xe	89.4	0.0581	FO	Xu et al. (2022)
Bi ₂ O ₃ /BiFeO ₃	Hydrothermal	p-n	18	0.5/0.4	60	9.0	300 W Xe/PMS	91.2	0.031	PFO	Liu et al. (2023b)
g-C ₃ N ₄ /BiOBr	Solvothermal	S-scheme	10	1.0	50	n/a	300 W Xe	100.0	n/a	n/a	Chen et al. (2019)
TaON/Bi ₂ MoO ₆	Hydrothermal	S-scheme	20	0.4	75	6.2	300 W Xe	92.7	0.0329	PFO	Li et al. (2022c)
BiOI/BiVO ₄ /g-C ₃ N ₄	Hydrothermal	Dual Z-scheme	10	1.0	120	n/a	65 W LED	89.0	0.0152	PFO	Zhu et al. (2022a)
CdIn ₂ S ₄ /Bi ₂ MoO ₆	Hydrothermal	S-scheme	20	0.05	90	6.8	300 W Xe	93.7	0.0247	QFO	Yao et al. (2024)
BiVO ₄ /CO ₃ ²⁻ -Bi ₂ O ₂ CO ₃	Hydrothermal	S-scheme	10	0.05	90	n/a	300 W Xe	78	0.021	PFO	Zhang et al. (2023b)
Ag/AgBr/BiOBr	Precipitation	S-scheme	10	0.5	90	8	85 W FL	74.0	0.016	PFO	Gupta et al. (2017)
g-C ₃ N ₄ /Bi ₂ WO ₆	Hydrothermal	S-scheme	10	0.4	120	n/a	300 W Xe	85.8	0.0096	PFO	Ma et al. (2023)
ZnFe ₂ O ₄ /Bi ₇ O ₉ I ₃	Hydrothermal	S-scheme	100	0.1	100	n/a	300 W Xe	95.1	n/a	PFO	Zhao et al. (2022)
Bi ₂ MoO ₆ -x/MoS ₂	Hydrothermal	S-scheme	20	0.05	25		Visible light	96.3	0.054	FO	Wei et al. (2024)
Ag/Bi ₂ MoO ₆ /ZnO	Hydrothermal	S-scheme	20	0.02	120	7	500 W Xe	84.0	0.0105	PFO	Li et al. (2024b)
Co ₃ O ₄ /Bi ₂ MoO ₆ @g-C ₃ N ₄	Hydrothermal	S-scheme	25	0.05	60	7	300 W Xe	95.2	0.0133	FO	Wei et al. (2023)
ZnMoO ₄ /Bi ₂ O ₄	Hydrothermal	S-scheme	15	0.02	120		300 W Xe	85.2	0.0191	PFO	Xing et al. (2022)
Bi ₂ WO ₆ /CuO	Hydrothermal	S-scheme	5	1.0	120	5	Sunlight	95.0	0.04806	FO	Wilson et al. (2025)
BiVO ₄ /CeVO ₄	Hydrothermal	p-n	50	0.05	300	n/a	150 W Xe	95.7	n/a	n/a	Lu et al. (2019)
BiOBr/CoFe ₂ O ₄	Solvothermal	S-scheme	20	1.0	120	n/a	65 W FL	90.0	0.0179	PFO	Zhu et al. (2022b)
Bi ₂ O ₃ /CuBi ₂ O ₄ /BiOBr	Solvothermal	Z-scheme	28	0.3	100	3-9	Sunlight	86.3	0.0103	PFO	Liu et al. (2024b)
CuFe ₂ O ₄ /Bi ₂ MoO ₆	Precipitation/Hydrothermal	S-scheme	10	0.3	60	7-9	300 W Xe	95.1	0.0117	PFO	Jia et al. (2024)
Bi ₂ Sn ₂ O ₇ /CuO	Hydrothermal	S-scheme	50	0.8	120	n/a	300W Xe	100.0	n/a	n/a	Fayazi et al. (2025)
BiOCl/Bi ₂ Fe ₄ O ₉	Hydrothermal	Type I	20	0.32	30	3.0	300W Xe	95.8	0.0934	PFO	Luo et al. (2025)
Sm ₆ WO ₁₂ /g-C ₃ N ₄	Hydrothermal	Type I	10	0.05	70		150 mW/cm ² T	90.8	0.034	FO	Prabavathi et al. (2021)
W and Cu vacancies on Bi ₂ WO ₆ /CuS	Hydrothermal	S-scheme	25	0.3-0.7	60	5-7	Visible light	90.5	0.2639	PFO	Xing et al. (2025)
Bi ₂ WO ₆ /C-Dots/TiO ₂	Hydrothermal	Z-scheme	10	0.075	90	7	Sunlight	88.3	0.0008	PFO	Sharma et al. (2020)

(continued on next page)

Table 2 (continued)

Photocatalysts	Type	Method	Reaction conditions					Degradation efficiency (%)	Rate constant (min ⁻¹)	Kinetic model	Ref.
			Drug conc. (mg/L)	Catalyst loading (g/L)	Treatment time (min)	pH	Light source				
Bi ₂ S ₃ @Zn-Co- cLDHs	Co- precipitation	Z- scheme	20	0.25-1.0	90		300 W MH	90.1	0.0280	FO	Tho and Nguyen (2025)
(BiOBr) _x / (Bi ₇ O ₉ I ₃) _{1-x}	Hydrothermal	S- scheme	50	1.0	120		400 W MH	95.4	0.0284	PFO	Fard et al. (2019)
CdS/Bi ₁₂ GeO ₂₀	Hydrothermal	Z- scheme	10	0.5	120		250 W Xe	80.0	0.0340	PFO	Ruan et al. (2019)

N.B.: Xe = Xenon bulb, T = Tungsten bulb, LED = light-emitting diode bulb, FL = Fluorescent bulb, and MH = Metal halogen bulb, TaON = tantalum oxynitride.

surface sites are not saturated and water/oxidant concentrations remain constant. It is effective for measuring degradation rates of pollutants like dyes. A plot of $\ln(C_0/C_t)$ versus t (min) yields a straight line with a slope of k . The QFO kinetic model describes photocatalytic degradation when pollutant concentration is low. The QFO and PFO kinetic models are generally considered the same, often used interchangeably to describe systems that are not truly first-order but behave as such only under specific conditions. Both are derived, non-ideal models used to describe reaction or adsorption rates that depend predominantly on one factor or reactant concentration, simplifying higher-order kinetics into a linear-like logarithmic form. For example, Fig. 3 shows the kinetics of the degradation reaction of CIP by Bi₁₂O₁₇Cl₂/UiO-66-NH₂ (Chu et al., 2024), Ag/AgBr/BiVO₄ (Chen et al., 2018a), and CdSe/Se/BiOBr (Du et al., 2022b) via the FO (a), LHFO (b), and PFO (c) kinetic models, respectively. Conversely, Fig. 4 shows the kinetics of the degradation reaction of LEV by Bi₃TaO₇/Mn_{0.5}Cd_{0.5}S or BMCS (Xu et al., 2022a), g-C₃N₄/BiVO₄/CuFe₂O₄ (Li et al., 2023), and CdIn₂S₄/Bi₂MoO₆ or CIS/BMO (Yao et al., 2024) via the FO (a), LHFO (b), PFO (c), and QFO (d) kinetic models, respectively.

4.4. Reaction rate

A high reaction constant value for a particular reaction indicates a reaction or degradation that proceeds very quickly, where the speed of the reaction is largely independent of the concentration of the reactants. Reactions with high reaction constant values reach equilibrium or

completion faster and require less activation energy. Table 1 shows the kinetic reaction constant of CIP by various bismuth-based heterojunctions. As discussed earlier, a true comparison of the reaction rate of various heterojunction photocatalysts for the degradation of CIP and LEV is difficult when various variables are different for studies carried out by different research groups. However, we simplified our comparison by ignoring those variables. Of these, Fe₃O₄/Bi₂WO₆ exhibited the highest rate of reaction for the photocatalytic degradation of CIP, as the reaction constant reached 0.557 (Zhu et al., 2021). The second-highest photodegradation performance was exhibited by Bi₂O₃/(BiO)₂CO₃, for which the reaction constant was 0.476 (Chen et al., 2018b). Conversely, BiFeO₃/BiVO₄ and cadmium-doped silver oxide (Cd-Ag₂O)/BiVO₄ showed the poorest performance, as the reaction constant was 0.005 and 0.009, respectively (Nkwachukwu et al., 2023; De et al., 2022). Table 2 shows the kinetic reaction constant of LEV by various bismuth-based heterojunctions. Of the various bismuth-based heterojunctions, Bi₂WO₆/CuS containing W and Cu vacancies showed the highest performance in terms of the reaction constant, as the reaction rate constant reached 0.2639 (Xing et al., 2025). BiOCl/Bi₂Fe₄O₉ also showed good performance, as the reaction rate constant reached 0.09 (Luo et al., 2025). Conversely, g-C₃N₄/Bi₂WO₆ showed quite poor performance, as the reaction constant was only 0.009.

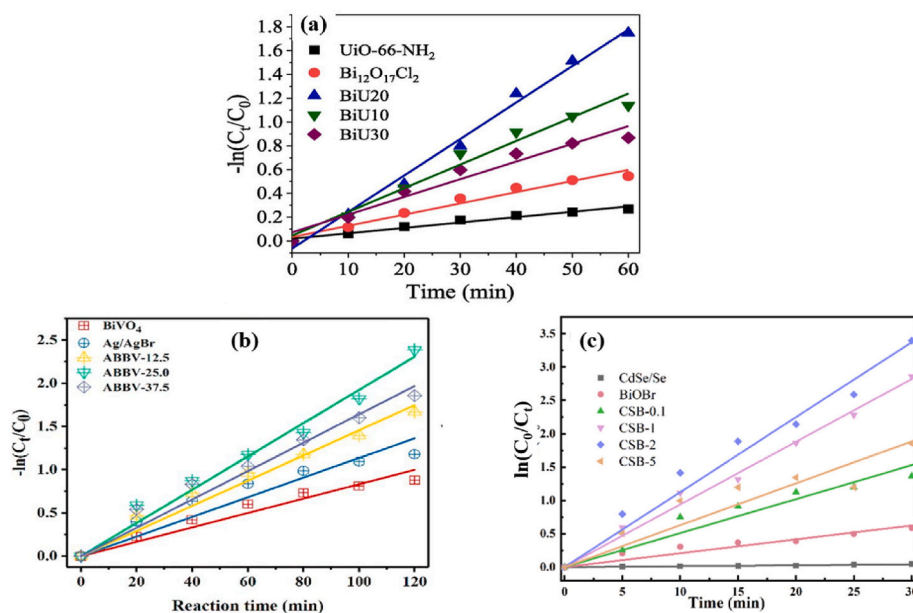


Fig. 3. (a) FO, (b) LHFO, and (c) PFO model degradation of CIP by Bi₁₂O₁₇Cl₂/UiO-66-NH₂ (Chu et al., 2024), Ag/AgBr/BiVO₄ (Chen et al., 2018a), and CdSe/Se/BiOBr (CSB) (Du et al., 2022b). Reproduced with permission from Elsevier.

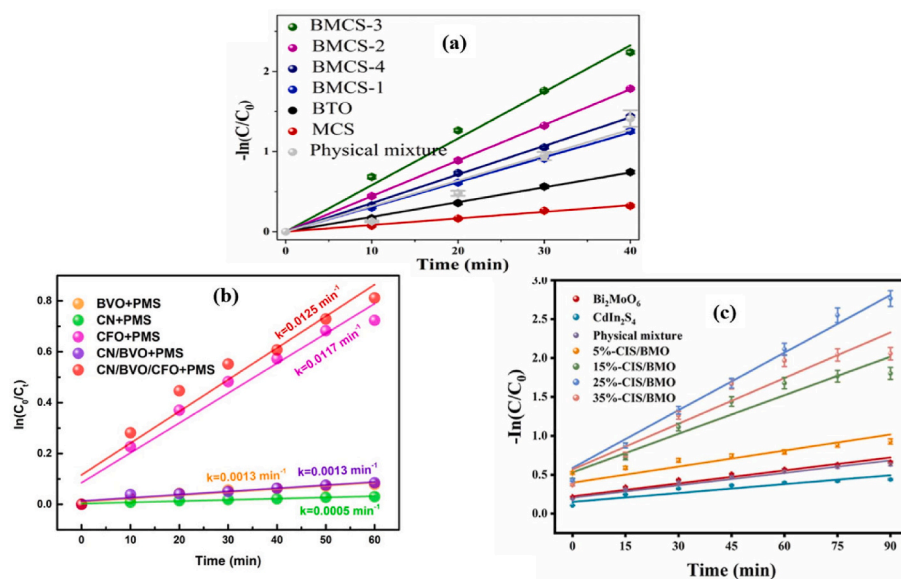


Fig. 4. (a) FO, (b) PFO, and (c) QFO model degradation of LEV by BMCS (Xu et al., 2022a), $g\text{-C}_3\text{N}_4/\text{BiVO}_4/\text{CuFe}_2\text{O}_4$ (Li et al., 2023), and CIS/BMO (Yao et al., 2024). Reproduced with permission from Elsevier.

4.5. Critical comparison and mechanistic insights from representative heterojunction systems

Bismuth-based heterojunctions have emerged as highly versatile and efficient photocatalysts for eliminating emerging environmental pollutants, specifically CIP and LEV. However, it is difficult to make a true comparison of the degradation performance of various bismuth-based heterojunction photocatalysts solely based on degradation percentage, as the reported efficiencies were obtained by various research groups under different experimental conditions, including antibiotic concentration, catalyst dosage, solution pH, light source, light intensity and wavelength, and reaction time. The data compiled in Tables 1 and 2 therefore provide a broad literature overview rather than a direct ranking of photocatalytic performance. For example, the degradation performance of CIP summarized in Table 1 employed pollutant concentrations ranging from approximately 5 to 50 mg/L, catalyst loadings from 0.02 to 1 g/L, and treatment time from 6 to 240 min under different irradiation conditions, including different light sources. Similarly, LEV degradation performance summarized in Tables 1 and 2 also used different catalyst concentrations, irradiation sources, reaction times, and, in several cases, additional oxidants such as peroxymonosulfuric acid. Rather than interpreting the tabulated degradation percentages independently, the reported systems can be compared mechanistically according to four interconnected factors: (i) visible-light utilization, (ii) charge carrier generation and effective separation, (iii) charge carrier transport from the bulk of the catalysts to their surface, and (iv) surface chemical reactions (surface electrons and holes react with adsorbed antibiotic molecules). To improve overall photodegradation performance, researchers modify catalysts to target these specific bottlenecks, and a change in only a single factor will severely limit the overall efficiency.

S-scheme heterojunctions exhibited better overall performance, structural stability, and practical viability in pollutant degradation compared to other heterojunctions. For the CIP degradation, the $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{WO}_6$ S-scheme heterojunction is a particularly notable example, which achieved 99.7% degradation within 15 min and exhibited a reported rate constant of 0.5571 min^{-1} , the highest value among the CIP systems compiled in Table 1 (Zhu et al., 2021). For the LEV degradation, two S-scheme heterojunctions, $g\text{-C}_3\text{N}_4/\text{BiOBr}$ and $\text{Bi}_2\text{Sn}_2\text{O}_7/\text{CuO}$, exhibited 100% degradation (Chen et al., 2019; Fayazi et al., 2025). The high activity can be interpreted in terms of the S-scheme configuration

consisting of an oxidation photocatalyst (OP) and a reduction photocatalyst (RP), in which interfacial charge transfer occurs via a step-like directional migration and recombination of photogenerated carriers driven by a built-in electric field, energy band bending, and Coulombic attractions. This leaves high-energy electrons and holes separated, preserving strong redox capabilities for generating reactive oxygen species, such as hydroxyl and superoxide anion radicals. In contrast, the $\text{N-CD}/\text{Bi}_2\text{MoO}_6/g\text{-C}_3\text{N}_4$ Z-scheme heterojunction also showed 99% degradation of CIP, but the reaction constant was only 0.13 (Dang et al., 2021). The $\text{Bi}_2\text{WO}_6/\text{PANI}$ p-n junction exhibited 98% degradation of CIP at a rate constant of 0.041 (Tahir et al., 2020). The bismuth(III) oxide/bismuth subcarbonate ($\text{Bi}_2\text{O}_3/(\text{BiO})_2\text{CO}_3$) p-n heterojunction achieved 93.4% CIP degradation within 30 min at a rate constant of 0.476 min^{-1} (Chen et al., 2018b). The high reaction rate suggests that efficient interfacial charge separation through the p-n junction and favorable surface redox processes can compensate for differences in charge-transfer configuration. Therefore, photocatalytic performance should be interpreted from the combined effects of band alignment, interfacial electric fields, charge-carrier lifetime, surface adsorption, and accessible redox potentials rather than from the heterojunction label alone. The dual Z-scheme $\text{Bi}_2\text{MoO}_6/\text{GQDs}/\text{TiO}_2$ system provides a more direct mechanistic example. Although its reported CIP degradation efficiency was 90.2% after 150 min, mechanistic analysis showed that photogenerated electrons in TiO_2 and Bi_2MoO_6 recombine preferentially with holes in the GQDs, leaving electrons in the GQDs conduction band and holes in the valence bands of TiO_2 and Bi_2MoO_6 (Lu et al., 2022). The remaining electrons participate in O_2 reduction to form $\bullet\text{O}_2^-$, whereas the retained holes promote $\bullet\text{OH}$ formation. Thus, the importance of this system lies not only in its removal efficiency but also in demonstrating how a multi-component architecture can preserve complementary reduction and oxidation potentials and thereby generate multiple reactive species.

For LEV degradation, the $\text{Bi}_2\text{WO}_6/\text{CuS}$ system containing W and Cu vacancies exhibited the highest reported reaction rate constant in the compiled dataset (0.2639 min^{-1}) (Xing et al., 2025), whereas $\text{BiO-Cl}/\text{Bi}_2\text{Fe}_4\text{O}_9$ (mullite-type bismuth ferrite) (Luo et al., 2025) and $g\text{-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ (Luo et al., 2026) showed substantially lower values of 0.09 and 0.009 min^{-1} , respectively. This comparison indicates that the heterojunction classification alone cannot explain the photocatalytic activity. Defect engineering can introduce additional electronic states, modify charge-carrier transport, increase the number of reactive sites,

and alter interfacial charge-transfer kinetics. Consequently, vacancy engineering and heterojunction formation should be considered complementary rather than independent design strategies.

The $\text{Bi}_2\text{MoO}_6/\text{MoS}_2$ S-scheme system further illustrates the importance of combining heterojunction engineering with defect or electronic-structure modification. A degradation efficiency of 96.3% was reported within only 25 min, suggesting rapid utilization of photogenerated charge carriers (Wei et al., 2024). In an S-scheme configuration, interfacial charge redistribution and the internal electric field selectively eliminate weakly reducing electrons and weakly oxidizing holes while preserving carriers with stronger redox potentials. This can increase the formation of reactive species capable of attacking LEV and can facilitate sequential oxidation of its piperazine and quinolone moieties.

Another mechanistically informative system is $\text{Co}_3\text{O}_4/\text{Bi}_2\text{MoO}_6/\text{g-C}_3\text{N}_4$. The reported mechanism involves formation of an internal electric field followed by directional carrier transfer, resulting in the accumulation of electrons in the conduction band of g- C_3N_4 and holes in the valence band of Bi_2MoO_6 . The conduction-band electrons reduce dissolved oxygen to $\bullet\text{O}_2^-$, while the valence-band holes oxidize surface hydroxide/water to $\bullet\text{OH}$. These reactive species subsequently attack LEV (Wei et al., 2023). This example demonstrates the direct link between heterojunction architecture, charge-carrier distribution, ROS generation, and molecular degradation.

Collectively, these representative systems demonstrate that photocatalytic performance is controlled by a hierarchy of interconnected properties rather than by heterojunction type alone. Heterojunction formation determines the possible charge-transfer pathway; band alignment and interfacial electric fields determine which charge carriers survive; defect states and surface structure influence carrier transport and adsorption; band-edge potential determines which ROS can be generated; and the resulting ROS and photogenerated holes determine the initial chemical transformations of CIP and LEV. Therefore, systems showing similar degradation percentages may operate through substantially different mechanisms, while systems with different nominal heterojunction classifications may achieve comparable activity when they provide efficient charge separation, suitable redox potentials, and accessible reactive sites.

Literature therefore does not support a simple relationship in which a particular heterojunction type always produces superior photocatalytic performance. No single heterojunction type (Type I, Type II, Type III, or Z-scheme) inherently guarantees superior photocatalytic performance because efficiency depends on a complex interplay of material

properties, reaction conditions, and kinetics. Instead, activity results from the interaction of band alignment, interfacial electric fields, charge-carrier lifetime, defect chemistry, surface adsorption, light absorption, and accessible redox potentials. For example, the $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{WO}_6$ S-scheme exhibits an exceptionally high CIP rate constant (Zhu et al., 2021), whereas the $\text{Bi}_2\text{O}_3/(\text{BiO})_2\text{CO}_3$ p-n heterojunction also shows a comparably high rate constant despite having a different charge-transfer configuration. Conversely, some nominally advanced Z- or S-scheme systems exhibit lower rate constants when charge transfer, surface accessibility, or reaction conditions are less favorable. Thus, heterojunction classification should be regarded as a mechanistic descriptor rather than a direct predictor of degradation efficiency.

5. Morphology and photodegradation mechanisms

5.1. Morphologies of various heterojunctions

The surface morphologies of various heterojunctions are usually characterized by scanning electron microscopy (SEM). Fig. 5 shows the SEM micrographs of various heterojunctions. Some of the heterojunctions show flower-like morphologies, and some of them show stacked or lamellar-like morphologies. The g- $\text{C}_3\text{N}_4/\text{BiOBr}/\text{Bi}_2\text{MoO}_6$ Z-scheme heterojunction prepared by the hydrothermal process showed flower-like spheres of Bi_2MoO_6 and cactus-like BiOBr dispersed in the g- C_3N_4 matrix (Fig. 5a). S-scheme 0D/3D heterojunction of $\text{Bi}_2\text{Sn}_2\text{O}_7/\text{SnS}_2$ shows sphere-shaped flower-like morphologies, in which case smaller $\text{Bi}_2\text{Sn}_2\text{O}_7$ nanoparticles tightly adhere to the larger SnS_2 microspheres, forming a 0D/3D hierarchical structure (Ji et al., 2026). Although the floral morphology of SnS_2 remains intact, its surface becomes roughened with the deposition of $\text{Bi}_2\text{Sn}_2\text{O}_7$ nanoparticles (Fig. 5b). The hydrothermally prepared Z-scheme $\text{CdSe}/\text{Se}/\text{BiOBr}$ shows a $\sim 2\ \mu\text{m}$ diameter hydrangea-like nanostructure (Fig. 5c), which is composed of many nanosheets with 30–40 nm thickness (Du et al., 2022a). The p-n heterojunction photocatalyst of 3D $\text{Ag}/\text{Ag}_6\text{Si}_2\text{O}_7/\text{Bi}_2\text{MoO}_6$ shows flower-like Bi_2MoO_6 microspheres formed by its 2D nanosheets, which are intimately and evenly decorated with ~ 15 – $30\ \text{nm}$ $\text{Ag}/\text{Ag}_6\text{Si}_2\text{O}_7$ nanoparticles (Fig. 5d) (Li et al., 2021a). The Z-scheme graphitic carbon nitride-decorated $\text{Bi}_2\text{MoO}_6/\text{g-C}_3\text{N}_4$ shows a layered structure of graphitic carbon nitride with large and numerous stacking nanosheets (Dang et al., 2021). 100–150 nm long rod-shaped Bi_2MoO_6 particles are homogeneously dispersed onto graphitic carbon nitride (Fig. 5e). The SEM image of S-scheme $\text{Cu}_3\text{SnS}_4/\text{L-BiOBr}$ heterojunction shows stable layered structures, where the Cu_3SnS_4 was grown onto L- BiOBr lamellar

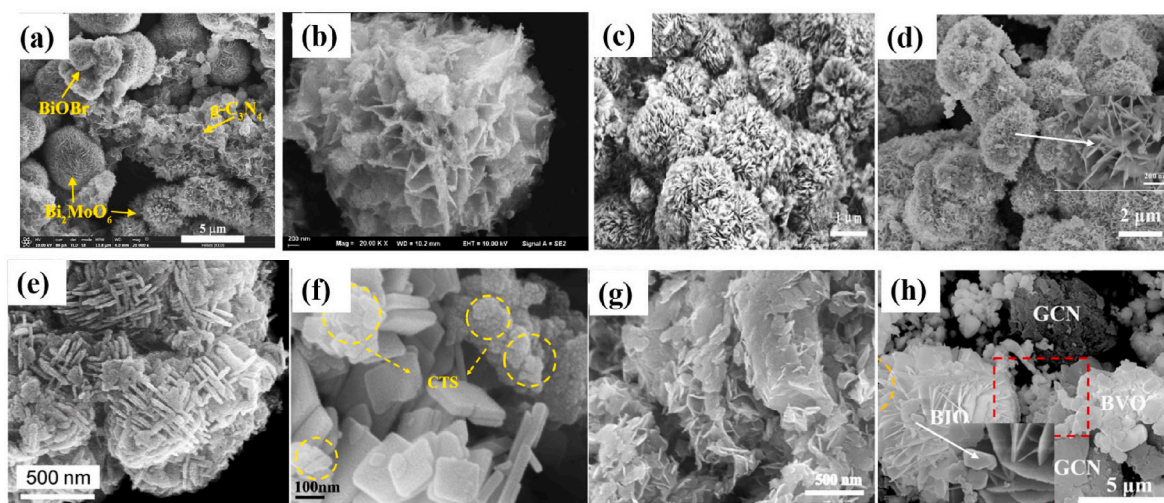


Fig. 5. SEM micrographs of (a) g- $\text{C}_3\text{N}_4/\text{BiOBr}/\text{Bi}_2\text{MoO}_6$ (Chankhanittha et al., 2024), (b) $\text{Bi}_2\text{Sn}_2\text{O}_7/\text{SnS}_2$ (Ji et al., 2026), (c) $\text{CdSe}/\text{Se}/\text{BiOBr}$ (Du et al., 2022b), (d) $\text{Ag}/\text{Ag}_6\text{Si}_2\text{O}_7/\text{Bi}_2\text{MoO}_6$ (Li et al., 2021a), (e) $\text{Bi}_2\text{MoO}_6/\text{g-C}_3\text{N}_4$ (Dang et al., 2021), (f) $\text{Cu}_3\text{SnS}_4/\text{L-BiOBr}$ (Li et al., 2022b), (g) $\text{Bi}_2\text{O}_2\text{S}/\text{Bi}_2\text{O}_3$ (Zheng et al., 2025), and (h) $\text{BiOI}/\text{BiVO}_4/\text{g-C}_3\text{N}_4$ (Zhu et al., 2022a). Reproduced with copyright permission from Elsevier.

nanosheets with a close contact interface (Fig. 5f). The morphology of Bi₂O₂S/Bi₂O₃ S-scheme heterojunction shows that the Bi₂O₂S nanosheets are densely and uniformly anchored on the surfaces of Bi₂O₃ nanorods, demonstrating that the rod-like Bi₂O₃ effectively prevents the agglomeration of Bi₂O₂S nanosheets (Fig. 5g) (Zheng et al., 2025). Conversely, the SEM micrograph of the BiOI/BiVO₄/g-C₃N₄ dual Z-scheme heterojunction shows a flower-globular-like structure. BiVO₄ is distributed on the surface of graphitic carbon nitride, and BiOI, as well as flower-globular BiVO₄, is in close contact with the layered graphitic carbon nitride (Fig. 5h) (Zhu et al., 2022a).

5.2. Photodegradation mechanisms

To understand the behavior of photocatalytic degradation of CIP and LEV, it is important to have a clear understanding of their molecular structures. These two antibiotics have a fluoroquinolone core with a carboxylic acid group at C-3, a carbonyl group at C-4, fluorine at C-6, and a piperazine group at C-7 (Ahadi and Emami, 2020). These sites are very susceptible to oxidative attack by photogenerated reactive species, such as electrons, holes, hydroxyl radicals ($\bullet\text{OH}$), and superoxide anion radicals ($\bullet\text{O}_2^-$), and are frequently the starting point of N-dealkylation reactions or of ring-opening reactions (Luo et al., 2023). Decarboxylation of the carboxyl group occurs under radical conditions, whereas hydroxylation and subsequent ring cleavage of the aromatic quinolone core occur with further oxidation in an advanced oxidation process (Sun et al., 2024). The strong C–F bond causes the oxidative potential to be demanding in the defluorination of the element to the later stages of degradation. Moreover, their amphoteric property and change in speciation based on pH affect the adsorption onto photocatalyst surfaces, which alters the reaction rate of reactive sites and the degradation process (Hamad, 2026).

Fig. 6 shows the chemical structures of CIP and LEV, and they have several functional groups in their molecular structures that are important in defining their photocatalytic degradation mechanisms. The piperazine ring is one of the most reactive sites, and it has nitrogen atoms that are highly susceptible to oxidative attack by photogenerated holes (h^+) and hydroxyl radicals ($\bullet\text{OH}$) (Li et al., 2022d). This oxidative reaction frequently causes degradation processes and may result in several changes, such as N-dealkylation, N-oxidation, and finally, opening the piperazine ring to produce several intermediate products. The other essential reactive site is the carboxyl group ($-\text{COOH}$) that is present on the quinolone backbone. This group is decarboxylated easily under radical-mediated oxidation to form carbon dioxide (CO_2) (Bellotti et al., 2023). The central aromatic heterocyclic framework of these antibiotics, comprising the quinolone core, can also be subject to extensive changes during photocatalysis (Sun et al., 2025b). This core structure is prone to hydroxylation, electrophilic attack by reactive oxygen species, as well as eventual heterocyclic ring cleavage under strong oxidative conditions, which gradually breaks down the molecular framework of the antibiotic. Also, CIP and LEV both have a relatively stable and resistant fluorine substituent (C–F bond), so defluorination is typically only observed in the more extreme stages of oxidation and is commonly regarded as a sign of profound degradation and mineralization (Leyva

et al., 2025). As an amphoteric compound, CIP has both acidic and basic functional groups that can protonate or deprotonate depending on the pH of the solution. It possesses two dissociation constants, 5.76–6.1 (pK_{a1}) and 8.6–8.8 (pK_{a2}), which means that CIP molecules are cationic below pH 5.76, anionic above pH 8.8, and neutral between pH 6.1 and 8.6 (Lima et al., 2025). Similarly, LEV also has two dissociation constants, 5.6–5.8 (pK_{a1}) and 7.9–8.7 (pK_{a2}), due to the presence of both an acidic and a basic functional group. This means that the surface of LEV molecules is cationic below pH 5.6, anionic above pH 7.9, and neutral between pH 5.6 and 7.9 (Czyrski, 2022). The point of zero charge (pH_{pzc}) of most of the heterojunction catalysts is around neutral pH, which means that CIP, LEV, and the heterojunction catalysts have similar charge in both acidic and alkaline conditions. Therefore, the maximum degradation of CIP and LEV occurs at the pH when the repulsive force between LEV and heterojunctions or CIP and heterojunctions is at a minimum, so that CIP or LEV molecules encounter the catalyst surface and degradation can occur by various active species generated by the catalyst under the light sources.

The electrons in the valence band get excited to the conduction band when photons with energy equivalent to or greater than the band gap are incident on semiconductors based on bismuth (Wang et al., 2026), such as BiVO₄, Bi₂WO₆, Bi₂MoO₆, or BiOX, with residual positively charged holes in the valence band. The product of this process is the formation of photogenerated charge carriers (e^-/h^+ pairs), which catalyze further redox reactions. Fig. 7a-d shows that the conduction band electrons that have been produced by the photogeneration process can react with dissolved oxygen molecules on the catalyst surface to form superoxide radicals ($\bullet\text{O}_2^-$), and the holes in the valence band can react with water molecules or surface hydroxyl groups to form hydroxyl radicals ($\bullet\text{OH}$). These reactive oxygen species (ROS), along with the oxidative holes themselves, are extremely reactive and are also a crucial factor in the degradation of antibiotic molecules. In most bismuth-based photocatalytic reactions, superoxide radicals ($\bullet\text{O}_2^-$) and photogenerated holes (h^+) are regarded as the main oxidative species, and hydroxyl radicals are added based on the valence band potential and reaction conditions (Yuan et al., 2025). The generation and involvement of these reactive species help a lot in increasing the oxidative destruction of pollutants by targeting their vulnerable functional groups in the molecules of the antibiotics, which consequently results in their conversion to smaller intermediates and final mineralization. Upon visible-light irradiation, bismuth-based semiconductors absorb photons and generate electron–hole pairs. The generation of reactive oxygen species, such as hydroxyl and superoxide radicals, during photocatalysis depends on the redox potentials of the semiconductor band edges relative to specific reaction potentials. The reduction of O_2 to superoxide radicals ($\text{O}_2/\bullet\text{O}_2^-$) requires a conduction band potential more negative than -0.33 V vs NHE, whereas the generation of hydroxyl radicals ($\text{OH}^-/\bullet\text{OH}$) requires a valence band potential more positive than $+1.99\text{ V}$ vs NHE (Xie et al., 2025).

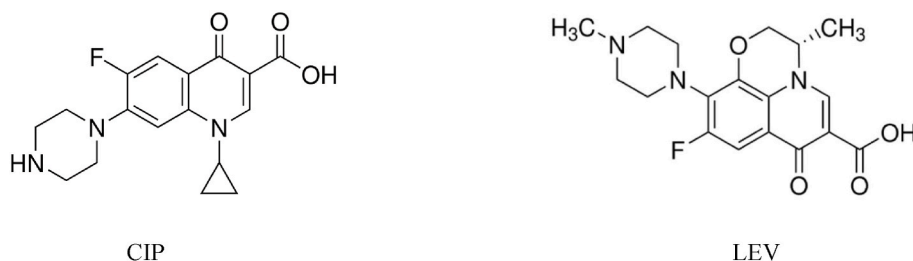


Fig. 6. Chemical structures of CIP (left) and LEV (right).

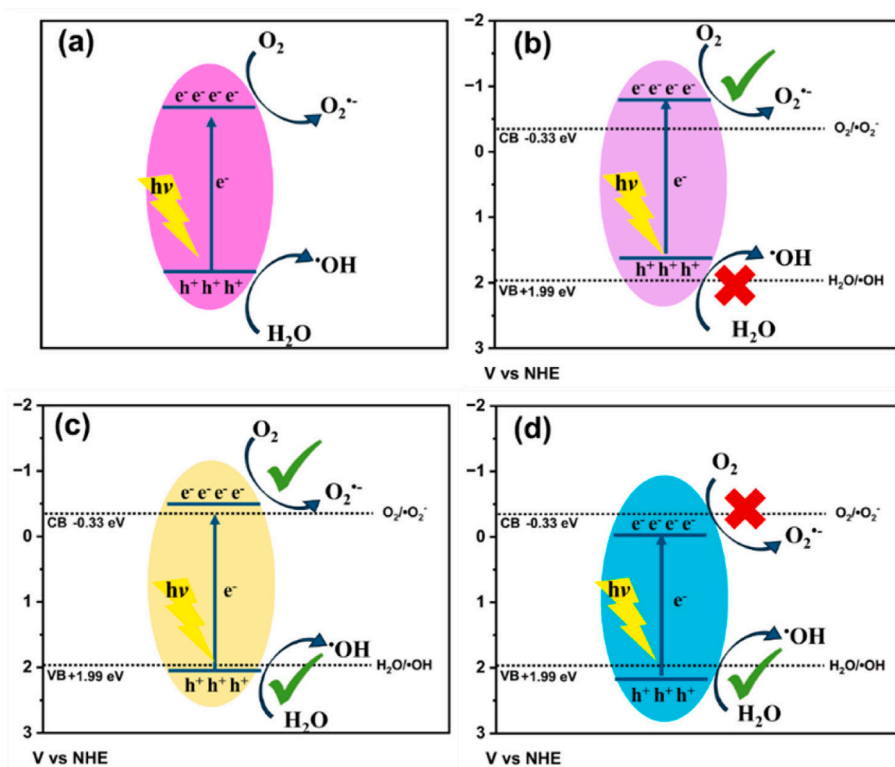
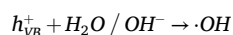


Fig. 7. The generation of reactive species on the surface of the photocatalyst is relative to their band positions.



[6]

The maximum production of the reactive oxygen species in the

bismuth-based photocatalysts is highly dependent on the position of band ends of the semiconductor vis-à-vis the redox potentials of the major reactions. Bi_2MoO_6 has a conduction band potential of

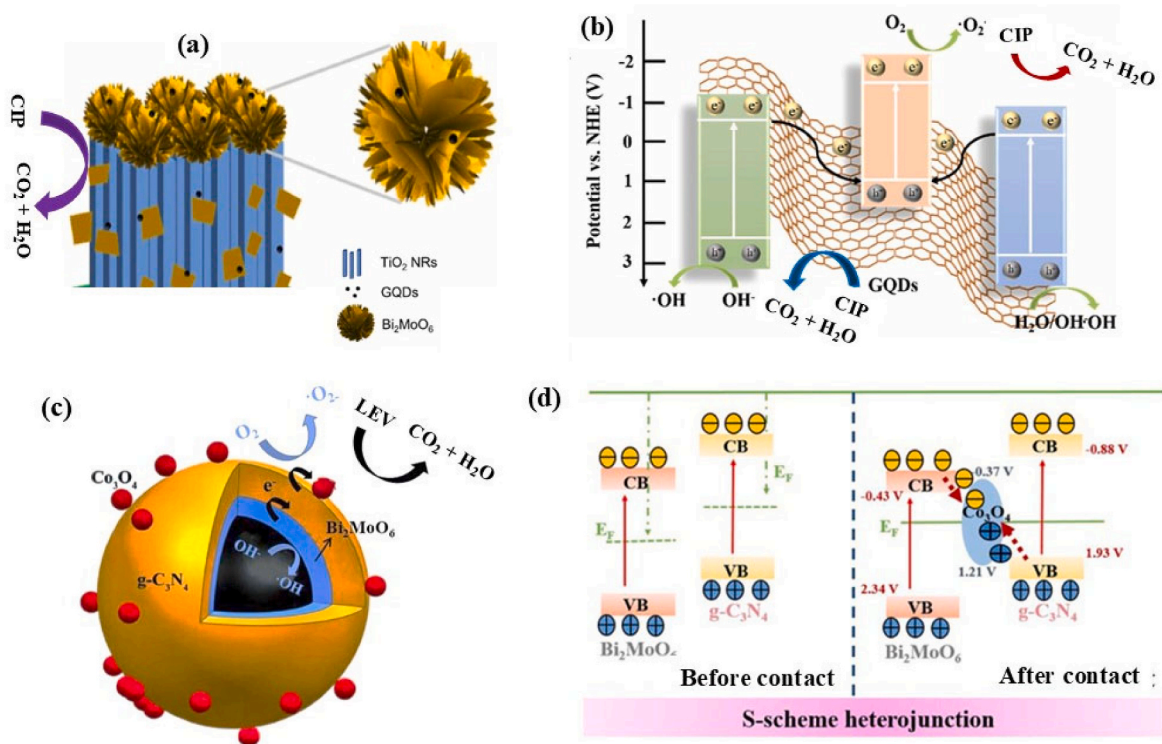
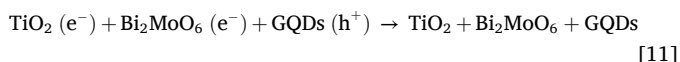
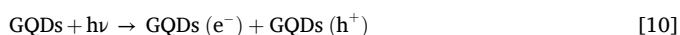
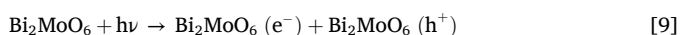
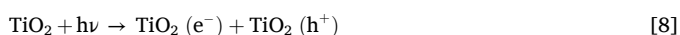


Fig. 8. Schematic diagram of formation of (a) dual Z-scheme Bi_2MoO_6 /GQDs/ TiO_2 nanostructured photocatalyst, (b) its photodegradation mechanism of CIP (Lu et al., 2022), and formation of (c) S-scheme $Co_3O_4/Bi_2MoO_6@g-C_3N_4$ microspheres, and its (d) photodegradation mechanism of LEV (Wei et al., 2023). Reproduced with permission from Elsevier.

approximately -0.33 V vs NHE, which is negative enough to reduce molecular oxygen to the $\bullet\text{O}_2^-$ radical (Fig. 7b), and superoxide species become the most significant oxidative species in most systems of Bi_2MoO_6 (Chen et al., 2025b). BiOCl exhibits a very negative conduction band potential (more negative than -0.33 V vs NHE), allowing the formation of superoxide radicals, while the valence band, which is more positive (more positive than $+1.99$ V vs NHE), is enough to produce hydroxyl radicals (Fig. 7c) (Wang et al., 2022). The conduction band potential of BiVO_4 is normally not suitable compared to the O_2/O_2^- reduction potential (-0.33 V). Therefore, electrons produced by photogeneration in BiVO_4 cannot effectively reduce oxygen to superoxide radicals. Nevertheless, the BiVO_4 valence band is very positive (greater than $+1.99$ V vs NHE), and this allows it to oxidize water or hydroxide ions to form hydroxyl radicals or oxidize organic pollutants directly (Fig. 7d) (Senasu et al., 2021). Similarly, Bi_2WO_6 displays a valence band potential more positive than 1.99 V vs NHE, permitting oxidation reactions, and its conduction band potential constrains the formation of superoxide (Karbasi et al., 2020). Such band edge potential differences are the driving force behind the fact that various bismuth-based photocatalysts generate different reactive species and hence have different degradation reactions of antibiotic molecules. Lu et al. described the photodegradation mechanism of CIP by a dual Z-scheme $\text{Bi}_2\text{MoO}_6/\text{GQDs}/\text{TiO}_2$ heterojunction, which is shown in Fig. 8a, b (Lu et al., 2022). The following empirical formula is used for measuring the band gap energy of semiconductors:

$$E_{CB} = E_{VB} + E_g \quad [7]$$

where E_{CB} is the conduction band edge potential, E_{VB} is the valence band edge potential, and E_g is the band gap energy. Lu et al. described the photodegradation mechanism of CIP by a dual Z-scheme $\text{Bi}_2\text{MoO}_6/\text{GQDs}/\text{TiO}_2$ heterojunction (Lu et al., 2022). The photogenerated electrons in the CBs of TiO_2 and Bi_2MoO_6 directly recombine with the holes in the VB of the GQDs, resulting in electrons being stored in the CB of the GQDs and holes in the VB of TiO_2 and Bi_2MoO_6 . The electrons in the CB of the GQDs can generate $\bullet\text{O}_2^-$, while the holes retained in the VB of TiO_2 and Bi_2MoO_6 can generate $\bullet\text{OH}$. The generation of various reactive species can be described by the following equations:



The $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals can attack CIP, degrading it to CO_2 and H_2O . On the other hand, Ma et al. described the photodegradation mechanism of LEV by S-scheme cobalt oxide (Co_3O_4)/ Bi_2MoO_6 @g- C_3N_4 hollow microsphere heterojunction, which is shown in Fig. 8 (c, d) (Wei et al., 2023). Ma et al. calculated that the valence band edge potentials for Bi_2MoO_6 and g- C_3N_4 are 2.34 eV and 1.93 eV, respectively, while the conduction band edge potentials are 0.43 eV and 0.88 eV, respectively (Ma et al., 2023). As the work function of Bi_2MoO_6 is greater than that of g- C_3N_4 , it can be expected that charge is transferred from Bi_2MoO_6 to g- C_3N_4 when the two materials are in contact until the Fermi energy level reaches equilibrium. After reaching equilibrium, an internal electric field (IEF) is formed at the interface from g- C_3N_4 to Bi_2MoO_6 , promoting the transfer of photogenerated electrons from the CB of Bi_2MoO_6

to the VB of g- C_3N_4 (Le et al., 2025). This promotes the transfer and separation of photogenerated carriers and improves the photocatalytic degradation performance. The use of Co_3O_4 nanoparticles as a surface-loaded co-catalyst in the $\text{Co}_3\text{O}_4/\text{Bi}_2\text{MoO}_6$ @g- C_3N_4 heterojunction microspheres enhances the photocatalytic efficiency by acting as an effective acceptor and trap for photo-induced charge carriers. This promotes the effective separation of photogenerated electrons and holes, resulting in the accumulation of holes in the VB of Bi_2MoO_6 and electrons in the CB of g- C_3N_4 . The E_{CB} of g- C_3N_4 is more negative than the standard redox potential $E(\text{O}_2/\bullet\text{O}_2^-)$, so electrons on the CB can react with O_2 to form $\bullet\text{O}_2^-$. The E_{VB} of Bi_2MoO_6 is greater than the standard redox potential $E(\text{OH}^-/\bullet\text{OH})$, so the holes on the VB can react with OH^- to form $\bullet\text{OH}$. Similarly, the $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals can attack LEV, degrading it to CO_2 and H_2O .

5.3. Unified framework linking heterojunction architecture, reactive species, and degradation pathways

The photodegradation of CIP and LEV over bismuth-based heterojunction photocatalysts can be understood through a unified sequence involving light absorption, interfacial charge transfer, ROS generation, molecular attack, and subsequent transformation of degradation intermediates. Although the detailed pathways vary according to the heterojunction architecture and the chemical structure of the antibiotic, the overall process is governed by the band alignment and interfacial charge-transfer characteristics of the photocatalyst. Upon visible-light irradiation, photons with energy equal to or greater than the band gap generate electron-hole pairs (Tuama et al., 2024). The subsequent migration of these carriers is determined by the heterojunction type and ultimately controls which electrons and holes remain available for surface redox reactions.

In conventional Type II heterojunctions, photogenerated electrons preferentially migrate toward the lower-energy conduction band, whereas holes migrate toward the higher-energy valence band. This spatial separation can suppress electron-hole recombination; however, it can also decrease the reduction and oxidation potentials of the surviving charge carriers. Consequently, the formation of highly reactive species may be restricted when the resulting band-edge potentials are insufficient to drive the corresponding redox reactions (Maheshwari et al., 2026). In contrast, Z-scheme and S-scheme architectures are designed to retain strongly reducing electrons and strongly oxidizing holes, thereby providing a more favorable combination of charge separation and redox capability. The manuscript's discussion of Z-scheme systems emphasizes the preservation of strong redox potential through selective recombination of low-energy carriers, whereas S-scheme systems achieve a similar functional outcome through interfacial charge redistribution and an internal electric field (Zhang et al., 2026c).

The retained charge carriers then determine the ROS pool available at the photocatalyst surface. In general, conduction-band electrons can reduce dissolved O_2 to superoxide radicals ($\bullet\text{O}_2^-$), whereas sufficiently positive valence-band holes can oxidize surface $\text{H}_2\text{O}/\text{OH}^-$ to generate hydroxyl radicals ($\bullet\text{OH}$), or can directly oxidize adsorbed antibiotic molecules. In the present review, the reduction potential required for $\text{O}_2/\bullet\text{O}_2^-$ formation is approximately -0.33 V versus NHE, while the $\text{OH}^-/\bullet\text{OH}$ oxidation process requires a valence-band potential more positive than approximately $+1.99$ V versus NHE. Therefore, heterojunctions possessing sufficiently negative conduction bands favor $\bullet\text{O}_2^-$ generation, whereas those possessing sufficiently positive valence bands can promote $\bullet\text{OH}$ formation and/or direct oxidation (Meng et al., 2026).

The generated ROS and photogenerated holes subsequently attack the most chemically susceptible sites of CIP and LEV. Both antibiotics contain a fluoroquinolone core, a carboxylic acid group, a carbonyl group, a fluorine substituent, and a piperazine moiety. The piperazine nitrogen atoms are particularly susceptible to oxidative attack, resulting in N-dealkylation, N-oxidation, and eventual piperazine-ring opening. Oxidative attack can also induce hydroxylation of the quinolone

structure, decarboxylation of the carboxyl group, cleavage of the heterocyclic framework, and, at more advanced stages of oxidation, defluorination (Sun et al., 2024). Therefore, the degradation process can be considered a cascade rather than a single reaction: heterojunction architecture determines charge-transfer direction; charge-transfer direction determines the surviving redox-active electrons and holes; their band-edge potentials determine the accessible ROS; and the ROS and holes determine the initial molecular transformations and subsequent degradation pathways. For both CIP and LEV, these transformations commonly involve oxidation of the piperazine group, hydroxylation and cleavage of the quinolone framework, decarboxylation, dealkylation/demethylation, and eventual defluorination, followed by formation of smaller organic intermediates and, when oxidation is sufficiently complete, mineralization toward CO_2 , H_2O , and inorganic products. A unified mechanistic framework for photodegradation of CIP and LEV by bismuth-based heterojunction photocatalysts is presented in Fig. 9.

5.4. Regeneration and recovery of spent photocatalysts

For economic viability and practical applications, the heterojunction photocatalysts must have easy regeneration for recycling and reuse many times. However, regeneration of photocatalysts is quite challenging, and after each recycling, they lose some level of photocatalytic efficiency. Heterojunction photocatalyst regeneration typically involves washing spent catalyst surfaces with organic solvents like acetonitrile and ethanol to remove adsorbed intermediates or pollutants. The most common regeneration methods are solvent washing, thermal treatment, oxidation with hydrogen peroxide, and in-situ photo-regeneration. Rinsing used catalysts with polar solvents (such as ethanol or acetonitrile) desorbs residual organic molecules from active sites. Mild calcination in air or an inert gas burns off or volatilizes stubborn carbonaceous deposits accumulated during pollutant degradation. Irradiating the heterojunction in a clean aqueous or sacrificial solution reduces accumulated surface species and restores active redox states.

Various factors affect the successful regeneration of heterojunction photocatalysts. The performance loss during recycling is frequently associated with the surface adsorption of contaminants rather than a

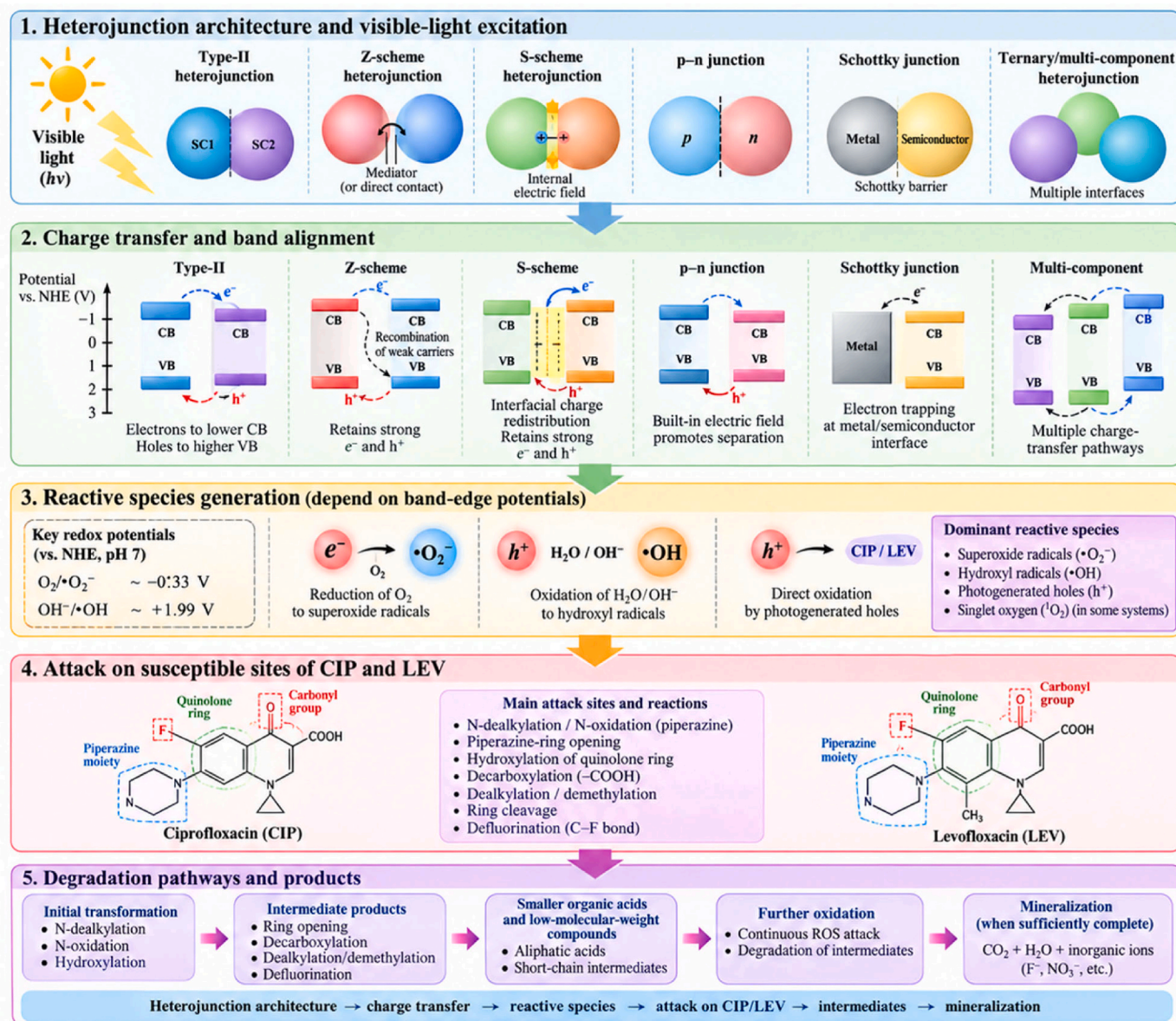


Fig. 9. Unified mechanistic framework for photodegradation of CIP and LEV by bismuth-based heterojunction photocatalysts.

breakdown of their core crystal structure. Built-in internal electric fields in advanced S-scheme or Z-scheme designs prevent severe photocorrosion during operation. While initial efficiency recovers well after washing, cumulative recycling and adsorption of contaminants can still cause a gradual drop in photocatalytic performance. Jan et al. studied recycling of the CdS/Cs₃Bi₂Br₉ photocatalyst with 30% hydrogen peroxide solution for 60 min after its application to the destruction of CIP. They found that the degradation performance of the catalyst for CIP dropped to 50% after the 5th cycle of regeneration (Jan et al., 2025).

6. Degradation products and ecotoxicity

Only a small number of published articles reported the photodegradation products of LEV and CIP by various bismuth-based heterojunction photocatalysts, and even a smaller number of articles reported the toxicity of various degradation products of CIP and LEV. However, the degradation products of such strong antibiotics deserve more attention due to the possible toxic effects these degradation products may have on human health, as well as our water and ecosystems.

6.1. CIP degradation products

For example, Lu et al. studied the photodegradation of CIP by a dual Z-scheme Bi₂MoO₆/GQDs/TiO₂ heterojunction photocatalyst and also outlined the possible degradation routes as illustrated in Fig. 10 (Lu et al., 2022). They found that a combination of hydroxyl radicals ($\cdot\text{OH}$), superoxide radicals ($\cdot\text{O}_2^-$), and h^+ (positive holes) was responsible for driving the CIP degradation process. They outlined three possible routes based on degradation products isolated, identified, and confirmed by liquid chromatography-mass spectrometry (LC-MS). In the first route, $\cdot\text{O}_2^-$ or $\cdot\text{OH}$ free radicals can attack the piperazine ring of CIP, causing ring-opening reactions that form intermediate P1 (m/z 306) and then replacement of piperazine with an amine and the removal of fluorine, forming P2 (m/z 245). P2 is then oxidized to a smaller product, P3 (m/z 123) or benzoic acid, via deamination and decarbonylation,

which is then degraded to CO₂ and water. On the other hand, the $\cdot\text{O}_2^-$ free radical can attack the piperazine ring of CIP, causing the opening of the piperazine ring, forming P4 (m/z 362), which then can follow two possible degradation routes. In the second route, P4 can convert into P5 (m/z 344) by the removal of fluorine atoms, which can further reduce to P6 (m/z 315). After which, it can convert into P2 (m/z 245) via destruction of the piperazine and then can follow route 1 for further degradation into CO₂ and water. In the third route, P4 loses its amino group and undergoes carbonylation to produce P8 (m/z = 290), which, after losing the F atom, can convert into P9 (m/z = 272). These intermediate products can further degrade into carbon dioxide and water.

Fan et al. studied the photodegradation of CIP by a Bi₂MoO₆/g-C₃N₄ S-scheme heterojunction and identified that the final degradation product of one possible route is quinoline, and in the other route, finally, a product with an empirical formula of C₁₀H₁₃NO₅ was produced (Fan et al., 2025). Based on various degradation products identified by LC-MS at different times of photodegradation, two possible routes of degradation are proposed (Fig. 11). The ring opening of piperazine by oxidation forms the product P1 (m/z 333.92) containing an amine ($-\text{NH}_2$) and carbonyl ($\text{C}=\text{O}$) groups on the alkyl amine nitrogen, which further degrades by two routes. In the first route, the removal of the fluorine atom of P1 causes the formation of product P2 (m/z 316), which is later converted by the cleavage of the $\text{C}=\text{O}$ bond to form product P3 (m/z 301.99). In the subsequent steps, product P4 (m/z 258.04) is formed via decarboxylation, and then product P5 (m/z 214.95) is formed by the cleavage of the C-N and C-C bonds. In the next step, through hydrolysis and deamination, the product P6 (m/z 202) and finally product P7, or quinoline, are formed by the removal of hydroxyl, carbonyl, and cyclopropyl groups. In the second route, P1, by cleavage of the C-N bond of P1, forms the product P8 (m/z 278.97), which is then converted into P9 (m/z 262.88) via decarboxylation and finally P10 (m/z 228.02) with an empirical formula of C₁₀H₁₃NO₅. After extending the photodegradation time, they were partially mineralized to H₂O and CO₂. As they did not measure the TOC reduction, it is difficult to evaluate how much of the degradation products of CIP were mineralized.

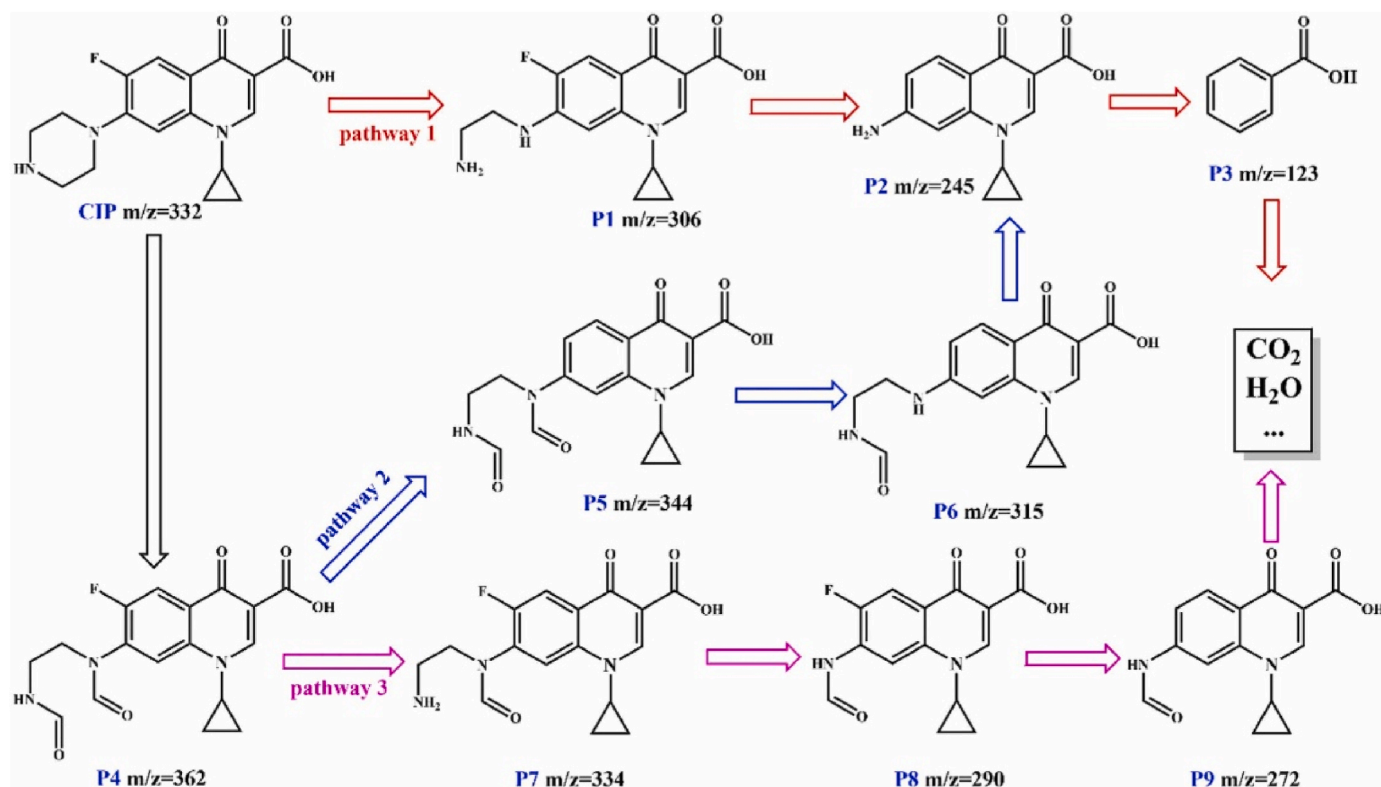


Fig. 10. Degradation pathways of CIP by Bi₂MoO₆/GQDs/TiO₂ heterojunction photocatalysts (Lu et al., 2022). Reproduced with permission from Elsevier.

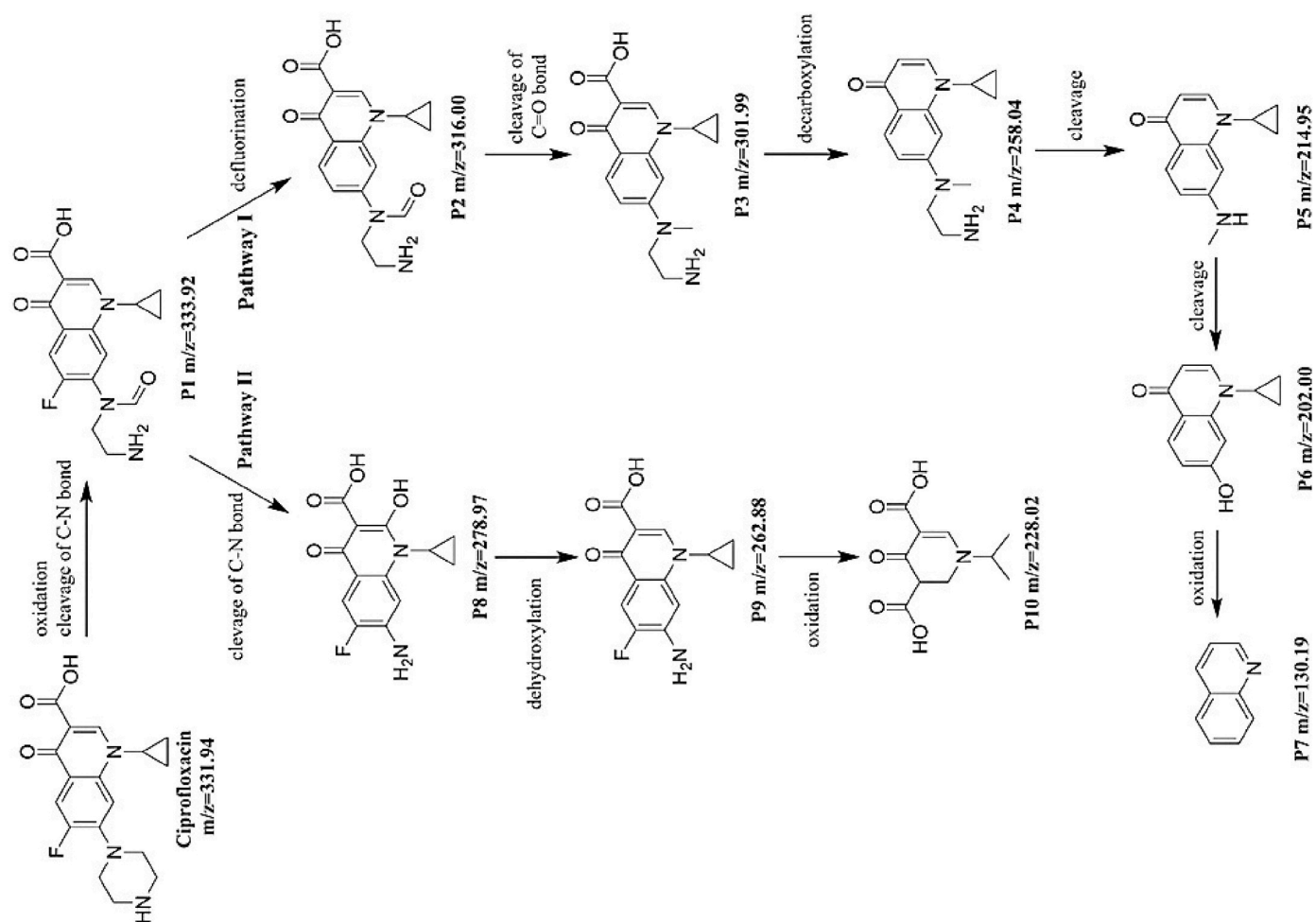


Fig. 11. Possible degradation routes of CIP photodegraded by $\text{Bi}_2\text{MoO}_6/\text{g-C}_3\text{N}_4$ S-scheme heterojunction photocatalyst (Fan et al., 2025). Reproduced with permission from Elsevier.

Similarly, Tu et al. proposed two reaction pathways in the CIP photodegradation by O-doped- $\text{g-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$ S-scheme heterojunction catalyst, and in both routes, the final product was benzoic acid (Chen et al., 2024a). The degradation products of CIP photodegraded by $\text{BiOBr}/\text{TiO}_2$, determined by gas chromatography-mass spectrometry (GC-MS), were 3-hydrobutan-2-one, 2-butanone, and phenol. With extended exposure, they may degrade to low-molecular-weight organic acids, including acetic and formic acids, and the final TOC reduction after 120 min exposure was $\sim 85.5\%$ (Liu et al., 2025a). In the photodegradation of CIP by the S-scheme $\text{Bi}_2\text{WO}_6/\text{NiO}$ heterojunction, one reaction route identified the final product as $\text{C}_4\text{H}_9\text{N}$, and the other two routes identified the final product as 1-phenylprop-2-en-one (Liu et al., 2022a). The final degradation intermediates of CIP photodegraded by an $\text{Ag}/\text{AgBr}/\text{BiVO}_4$ photocatalyst, identified by LC-MS, were unknown compounds with empirical formulas of $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_4$, $\text{C}_{16}\text{H}_{18}\text{FN}_3\text{O}$, and $\text{C}_{10}\text{H}_2\text{FNO}_3$ in the proposed various routes (Chen et al., 2018a). The low TOC removal (52.3%) shows incomplete CIP mineralization and the production of high-molecular-weight degradation products. On the other hand, the degradation products of CIP photodegraded by a non-stoichiometric bismuth oxychloride/amine-functionalized zirconium-based metal-organic framework ($\text{Bi}_{12}\text{O}_{17}\text{Cl}_2/\text{UiO-66-NH}_2$) Z-scheme heterojunction were 1,3-cyclohexanediamine, ethylene glycol, and other unknown compounds with formulas of $\text{C}_8\text{H}_5\text{FNO}_3$ and $\text{C}_{10}\text{H}_8\text{NO}_3$ (Chu et al., 2024). The degradation products of CIP by $\text{Bi}_2\text{MoO}_6/\text{g-C}_3\text{N}_4$ S-scheme heterojunction with oxygen vacancies were identified as quinoline and an unknown compound (Fan et al., 2025).

6.2. LEV degradation products

Wei et al. reported the three possible degradation routes for photodegradation of LEV by a $\text{Bi}_2\text{MoO}_{6-x}/\text{MoS}_2$ S-scheme heterojunction photocatalyst based on isolation and determination of degradation products at various stages by liquid chromatography-mass spectrometry (LC-MS) (Wei et al., 2024). In the first possibility, the ring-opening of the piperazine occurs, forming Product P1 ($m/z = 391$), which subsequently undergoes step-by-step degradation, demethylation, and decarboxylation, finally forming 2-fluoroaniline (Fig. 12). In the second possible route, demethylation and defluorination occur, forming hydroxyl and carboxyl groups, respectively, which further degrade to Product P5, which was then attacked by holes (h^+), generating Product 6 ($m/z = 290$) via a decarboxylation process. It was then decarboxylated and underwent ring opening of piperazine, forming Product P7 ($m/z = 261$). In the third possible route, the decarboxylation reaction of methyl morpholine in LEV converted it into Product P8 ($m/z = 334$), with further degradation of the N-methyl piperazine ring, which formed Product P9. With further degradation, P9 converted to P10 and finally into P11. They also identified and produced a series of small molecules, such as CO_2 , H_2O , fluorine, and ammonium ions, suggesting partial degradation of LEV. The final products, such as 2-fluoroaniline and other degradation products, could be highly toxic.

Fig. 13 shows the four possible degradation pathways in the case of photocatalytic degradation of LEV by $\text{Co}_3\text{O}_4/\text{Bi}_2\text{MoO}_6/\text{g-C}_3\text{N}_4$ (Wei et al., 2023). The authors proposed four possible degradation routes. The reactions involved in the degradation of LEV are demethylation,

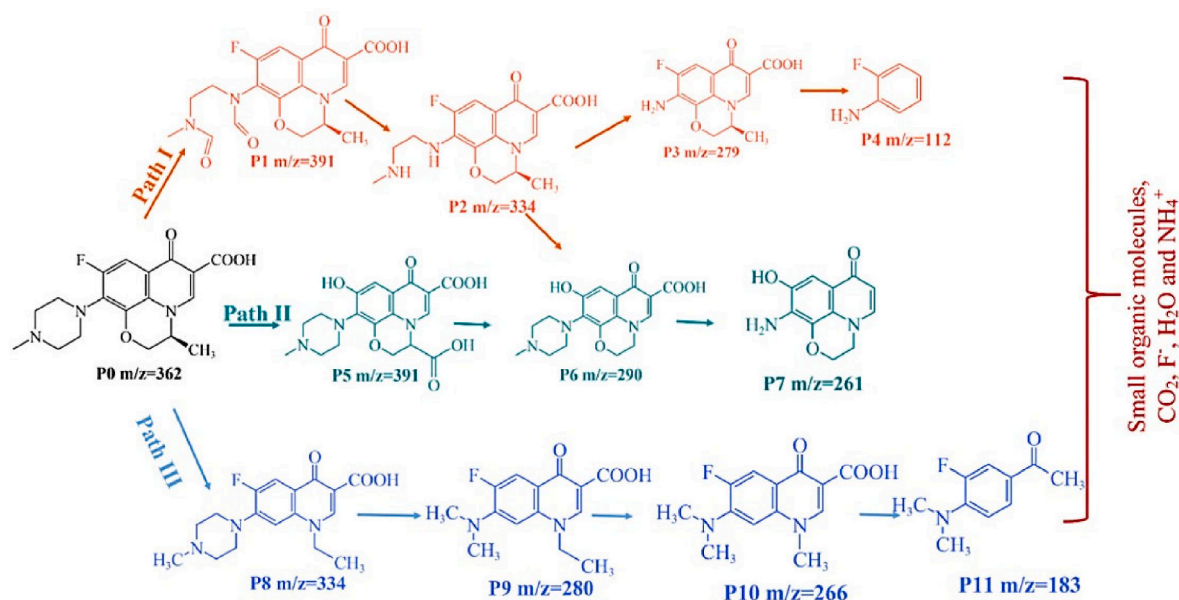


Fig. 12. Degradation routes of LEV photodegradation by $\text{Bi}_2\text{MoO}_{6-x}/\text{MoS}_2$ S-scheme heterojunction photocatalyst (Wei et al., 2024). Reproduced with permission from Elsevier.

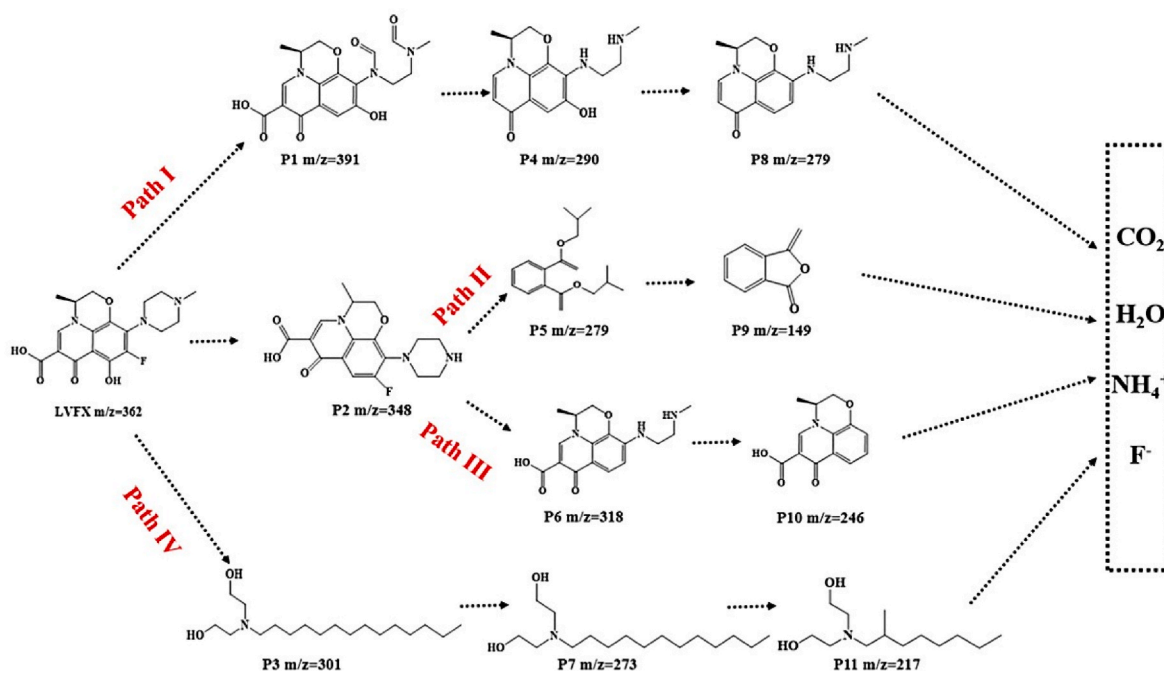


Fig. 13. Degradation routes of LEV photodegradation by $\text{Co}_3\text{O}_4/\text{Bi}_2\text{MoO}_6@\text{g-C}_3\text{N}_4$

ring opening of piperazine, and carboxylation. In the first route, ring opening of the piperazine of LEV occurs through free radical oxidation, and defluorination also occurs, forming product P1 ($m/z = 391$), which is then converted into product P4 ($m/z = 290$) containing two imino groups via decarboxylation and decarbonylation. In the next step, the hydroxyl group of P4 is lost, forming a final product P8 ($m/z = 279$). LEV can also form product P2 ($m/z = 348$) via dehydroxylation, which can then undergo degradation via two routes. In the second route, P2 undergoes an extensive oxidation reaction, causing ring opening of morpholine and piperazine, and also decarboxylation and decarbonylation, forming product P5 ($m/z = 279$), which is the next step that forms the final product P9 ($m/z = 149$) or a phthalide compound. In the third route, the piperazine of P2 can under ring opening reaction via

oxidation, forming product P6 ($m/z = 318$), which can further oxidize to finally form product P10 ($m/z = 246$). The final products produced by different routes are Products P8 ($m/z = 274$), P9 ($m/z = 149$), P10 ($m/z = 246$), and P11 ($m/z = 217$). They are then converted into smaller molecules as mentioned earlier.

S-scheme heterojunction photocatalyst (Wei et al., 2023). Reproduced with permission from Elsevier.

The degradation products of LEV by $\text{Bi}^0/\text{CN-G/BWO}$, identified by high-performance liquid chromatography-mass spectrometry (HPLC-MS), were low-molecular-weight fumaric acid, maleic acid, and oxalic acid, showing excellent mineralization (Lv et al., 2025). The degradation intermediates of LEV photodegraded by $\text{Bi}_3\text{TaO}_7/\text{Mn}_{0.5}\text{Cd}_{0.5}\text{S}$ were pyruvic acid, fluoromalononic acid, and 3-fluoro-7-methylimidazo[1,2-a]

pyridine-2-carboxylate (Liu et al., 2023b). The photodegradation of LEV by BiOI/BiVO₄/g-C₃N₄ dual Z-scheme heterojunction produced various intermediate products, such as 1-methylpiperazine and unknown organic compounds with an empirical formula of C₁₁H₉FN₂O and C₆H₉NO₂ (Zhu et al., 2022a). The total TOC removal efficiency over 120 min of exposure was only 32.8%. The degradation products of LEV by the CdIn₂S₄/Bi₂MoO₆ S-scheme heterojunction, predicted by four different routes, are diamino carbonyl-benzene, phthalic anhydride, and various unknown compounds with empirical formulae of C₁₁H₁₀O₂N₂ and C₁₀H₈O₃N₂ (Yao et al., 2024). The photodegradation of LEV by Bi₂O₃/CuBi₂O₄/BiOBr in the presence of PMS produces a range of unknown compounds with empirical formulae of C₁₇H₂₀FN₃O₃, C₁₂H₁₀FN₂O₂, and C₁₂H₁₂N₂O₂ (Liu et al., 2024b). LEV photodegraded by a CuFe₂O₄/Bi₂MoO₆ heterojunction produced 1-methylpiperazine, *trans*-2,3-dimethylacrylic acid, and an unknown compound, along with various low-molecular-weight chemical compounds, such as H₂O, CO₂, F⁻, NO₃⁻ and NH₄⁺ (Jia et al., 2024). Similarly, the degradation of LEV by BiOCl/Bi₂Fe₄O₉ with oxygen vacancies in the presence of PMS produced various unknown compounds (Luo et al., 2025).

Various degradation products identified in the photodegradation of CIP and LEV by various bismuth-based heterojunction photocatalysts discussed earlier were probably measured in the middle of the photodegradation treatment, not at the end of the treatment when the maximum degradation of these antibiotics occurred, to identify the degradation pathways. No published article reported analyses of degradation products of these antibiotics in the final treated water. However, several articles reported a 50 to 85% reduction in TOC of the post-treated water contaminated with these two antibiotics, suggesting the persistence of many of these intermediates in the treated water, which could be dangerous for humans and ecosystems.

6.3. Toxicity of the CIP and LEV degradation products

The ultimate goal of any photodegradation for treating toxic organic chemicals is their complete mineralization, i.e., degrading them into harmless end-products, such as carbon dioxide and water. The production of any persistent intermediate products is undesirable, as these intermediate degraded products could be more toxic than the parent drugs. The toxicity of the degradation products of antibiotics reported in various published articles was assessed by various simulated models, such as Ecological Structure-Activity Relationships (ECOSAR), Quantitative Structure-Activity Relationships (QSAR), and the Toxicity Estimation Software Tool (TEST). Chen et al. studied the acute and long-term toxicity of CIP photodegraded by Ag₃VO₄/CuCo₂O₄/Bi₄O₅Br₂ and its photocatalytic degradation intermediates to fish, daphnia, and green algae using the ECOSAR model (Chen et al., 2026). They found that all degradation products showed no acute toxicity to the mentioned test organisms. However, some of the decomposition products showed harmful chronic toxicity to aquatic organisms. Lu et al. estimated the

mutagenicity and bioconcentration factor of CIP photodegraded by the Bi₂MoO₆/GQDs/TiO₂ heterojunction photocatalyst by using the TEST model as represented in Fig. 14 (Lu et al., 2022). The bioconcentration factor (BCF) here is the concentration of CIP in an organism (e.g., fish tissue) divided by its concentration in the surrounding water at steady state, and it indicates the potential for bioaccumulation of CIP. They found that most of the degradation products of CIP showed lower mutagenicity compared to CIP. The bioconcentration factor of all intermediates was inferior to CIP, suggesting that the breaking of the piperazine ring caused a loss of toxicity. They also observed similar results in the case of CIP photodegraded by Bi₄O₅I₂/glucose-modified Bi₂O₂CO₃ and found that the toxicity of the CIP degradation products decreased significantly (Lu et al., 2025). However, Chu et al. reported that, based on QSAR model testing, most of the degradation products of CIP by Bi₁₂O₁₇Cl₂/UiO-66-NH₂ photodegradation exhibited LC₅₀ values harmful to toxic levels against *Daphnia magna* and fathead minnow, and some showed positive mutagenicity (Chu et al., 2024). Most of the degradation products of CIP photodegraded by the Bi₅O₇I/UiO-66-NH₂ heterojunction photocatalyst showed toxic-level LC₅₀ values against *Daphnia magna*, harmful-level BF, and some of them showed positive mutagenicity and strong developmental toxicity (Zhao et al., 2021). Some of the degradation products of CIP photodegraded by the Bi₁₂O₁₇Cl₂/UiO-66-NH₂ Z-scheme showed a toxic-level LC₅₀ value against *Daphnia magna*, and mutagenicity was positive, but the BF was positive (Chu et al., 2024).

On the other hand, the toxicity of degradation intermediates of LEV photodegraded by Bi⁰/CN-G/BWO, assessed by the TEST and QSARs, showed that the toxicity against fathead minnows and mutagenicity of the degradation products decreased with an increase in photodegradation time, but they were more prone to bioaccumulation (Lv et al., 2025). The toxicity of intermediate degradation products of LEV photodegraded by Bi₃TaO₇/Mn_{0.5}Cd_{0.5}S decreased, but they were still toxic to some extent, showing that the photodegraded CIP is still harmful (Xu et al., 2022a). The degradation intermediates of LEV photocatalyzed by TaON/Bi₂MoO₆ core-shell S-scheme heterojunction showed toxicity against fathead minnow, and most of them also exhibited mutagenicity (Li et al., 2022c). The toxicity of degradation products of LEV photodegraded by Bi₂O₃/CuBi₂O₄/BiOBr in the presence of PMS, assessed by TEST, showed toxic to very toxic LC₅₀ against fathead minnow, but oral rat LD₅₀ (48 h) was lower than that of the parent LEV (Liu et al., 2024b). The toxicity testing of degradation intermediates of LEV photodegraded by BiOCl/Bi₂Fe₄O₉ with oxygen vacancies in the presence of PMS shows less toxicity to green algae, *Daphnia magna*, and fish compared to LEV (Luo et al., 2025). The decomposition products of CIP and LEV are photodegraded by various bismuth-based heterojunction shows from low to high toxicity against rats, *Daphnia magna*, fathead minnow, and green algae, depending on the degradation products produced, as assessed by simulation using ECOSAR and TEST models. No published article reported the toxicity of the treated water contaminated with

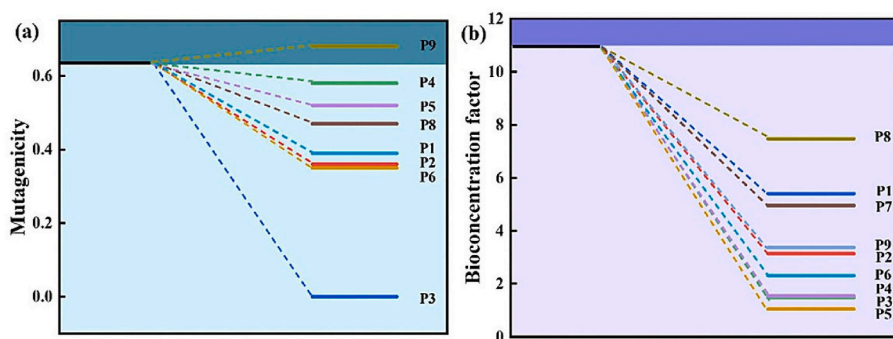


Fig. 14. (a) Mutagenicity and (b) bioconcentration factor of photodegraded products of CIP by Bi₂MoO₆/GQDs/TiO₂ heterojunction photocatalyst (Lu et al., 2022). Reproduced with permission from Elsevier.

these antibiotics and the toxicity of their degradation products to real organisms; therefore, the reliability of such results is uncertain.

No published article reported the toxicity of degradation products of CIP and LEV photodegraded by heterojunction photocatalysts using real organisms other than testing against various types of bacteria. For example, the toxicity testing of CIP solution degraded by Ag-Bi/CdS heterojunction under sunlight was tested against *S. aureus* and *E. coli* (Chakinala and Gogate, 2025). The untreated CIP solution exhibited strong toxicity against both types of bacteria, but the treated solution showed no activity against *E. coli* and very weak activity against *S. aureus*, suggesting the degradation products were non-toxic. Chen et al. found that the toxicity of CIP was reduced to 39.4% after 150 min photodegradation by Bi₂O₃/(BiO)₂CO₃ heterojunction (Chen et al., 2018b). The toxicity of intermediate products of LEV photodegraded by BaTiO₃/CdIn₂S₄ heterojunction showed no toxicity against *E. coli* (Tong et al., 2026). The toxicity of degradation products of LEV photodegraded by Co₃O₄/Bi₂MoO₆@g-C₃N₄ for 35 min increased when tested against *V. Fischeri* bacteria, suggesting that some intermediates were initially formed that were more toxic than LEV, but further photodegradation to 50 min decreased the toxicity (Wei et al., 2023).

7. Challenges and future perspectives

Although certain milestones have been achieved in recent years, there are still a number of challenges that have to be overcome to allow the use of bismuth-based photocatalysts for the removal of antibiotics from effluent. Primarily, the majority of studies are performed in the laboratory using unnatural antibiotic solutions under conditions that are not fully relevant to real-life wastewater matrices. Bismuth-based heterojunction photocatalysts offer strong visible-light absorption, but their practical application faces significant challenges, such as fast photo-generated charge carrier recombination, low quantum efficiency, poor long-term stability, and scalability issues. Key challenges include managing the balance between broad light absorption and redox capacity, optimizing interface charge transfer, and overcoming environmental risks like metal leaching into the treated effluent. Moreover, the scalability of heterojunction photocatalysts is limited by complex synthesis methods, high costs of specialized nanomaterials, and challenges in maintaining structural stability and recyclability during large-scale operation. Scaling up the synthesis of such catalysts often fails to deliver high solar-to-energy efficiency, as exhibited by lab-synthesized versions of the same catalysts because bulk interfaces lack continuous, intimate contact.

Another challenge is the deactivation of heterojunction photocatalysts, which occurs when structural, chemical, or physical changes at the material interface reduce the efficiency of charge separation and active site availability over time. Deactivation can occur for various reasons, such as the accumulation of carbonaceous by-products or refractory reaction intermediates on the catalyst surface blocks active sites and inhibits electron-hole pair transfer. Heterojunction boundaries can break down due to ion migration, phase transformations, or the irreversible accumulation of inactive surface species. Component semiconductor materials undergo self-oxidation or self-reduction reactions under illumination, destroying the active crystal lattice. High local operating temperatures cause particle growth and a subsequent loss of active surface area during sintering. The loss of vital functional groups, such as surface hydroxyls on metal oxides like TiO₂, diminishes radical generation.

Future studies should aim to assess the effectiveness of photocatalytic activities under complicated environmental conditions with multiple contaminants, inorganic ions, and natural organic matter, which could have a considerable effect on the degradation capability. Secondly, the mechanistic theory of charge transfer processes in complex heterojunction systems is not complete. The techniques of more advanced characterization, like in situ spectroscopy, transient absorption spectroscopy, and density functional theory (DFT) calculations,

should be used to learn more about photocatalytic processes and interfacial charge transfer processes. Lastly, the application and practicality of the photocatalytic systems are still in the pilot stage. Future research needs to consider photocatalytic reactor design, catalyst immobilization, long-term stability, and reusability in continuous flow. Besides that, photocatalysis can be combined with other sophisticated oxidation processes or membrane technologies, which are also likely to enhance the efficiency of antibiotic removal.

Future bismuth-based heterojunction photocatalysts are shifting toward the utilization of the full spectrum of solar light, S-scheme charge transfer mechanisms, and 2D/2D structural engineering to maximize their photocatalytic efficiency in pollutant degradation and energy conversion. Future research should focus on improving charge separation, maintaining high redox potential, green synthesis methods, lowering costs, ensuring long-term stability and recyclability, and solving scalability, stability, and industrial applicability issues. The performance of this type of heterojunction photocatalyst can be enhanced by designing heterojunctions utilizing machine learning and computational simulations (e.g., DFT) to predict highly efficient catalyst compositions before synthesis. Light absorption efficiency of the heterojunctions can be enhanced by incorporating surface plasmon resonance (SPR) effects from Bi metal and implementing defects/doping (Zhang et al., 2025). To accelerate charge transport, face-to-face 2D/2D bismuth-based heterojunctions need to be developed to provide larger contact areas.

The ecotoxicity of the degradation products of these antibiotics deserves more consideration, as they are rarely completely mineralized by photocatalytic degradation. Some intermediate products are created during their photodegradation that may become persistent and may have greater environmental concern compared to the parent antibiotics. Environmental impacts of these intermediate products were assessed mainly by using various in silico methods (e.g., ECOSAR, QSAR, and TEST) instead of using real organisms. These methods are increasingly used to comply with the 3Rs principle (Replacement, Reduction, Refinement) to replace animal testing in regulatory, pharmaceutical, and chemical safety regulations (e.g., REACH). They rely on high-quality training data; results could be affected due to their inability to fully replicate complex biological systems and potential lack of transparency in algorithms. They often fail to capture accurate in vivo bioavailability, require experimental validation, and face challenges with protein flexibility and structural uncertainty (Rivero-Pino et al., 2023; Al-Mohaya et al., 2024). There is also a lack of data available in published literature regarding the final compositions of the treated water contaminated with these antibiotics. Therefore, future research should shed light not only on the detection of toxic antibiotic intermediates by such photocatalysis but also on their concentration in the final treated water.

8. Conclusions

In the present review, the latest progress on the photodegradation of fluoroquinolone antibiotics, especially CIP and LEV, by various bismuth-based visible-light-driven heterojunction photocatalysts was summarized. The rising use of these antibiotics in water bodies is potentially a major ecological and human health hazard, as they are persistent and may cause antibiotic resistance. Photocatalysts made of bismuth have gained a lot of interest due to their narrow band gaps and good to high redox potentials. Of these methods, Z-scheme and S-scheme heterojunction systems have exhibited the most promising performance as they retain highly oxidative holes and strongly reductive electrons and thus enable the production of reactive oxygen species such as superoxide radicals ($\bullet\text{O}_2^-$) and hydroxyl radicals ($\bullet\text{OH}$). These reactive species play a key role in the breakdown of CIP and LEV in a cascade of oxidative reactions, such as oxidation of the piperazine ring, hydroxylation of the quinolone skeleton, decarboxylation, defluorination, and mineralization of the molecules to small inorganic molecules. The development of multi-component heterostructures, carbon-based functionalization,

defect engineering, and loading by noble metals further improved photocatalytic activity by overcoming limitations of traditional photocatalysts. The photodegradation efficiency of heterojunctions for the degradation of CIP and LEV varies depending on several interconnected material properties (e.g., electronic and structural properties, charge separation efficiency, and porosity) and various environmental factors. The degradation products of CIP and LEV by several heterojunctions also showed increased toxicity. Therefore, the selection of the right catalyst is absolutely critical to achieve high degradation of CIP and LEV to environmentally benign compounds. Scalability, catalyst regeneration, and cost are the primary barriers keeping laboratory photocatalysis from widespread industrial deployment. It is anticipated that after solving various issues, bismuth-based heterojunction photocatalysts will be used in industry, not only for environmental remediation but also for hydrogen energy generation.

CRediT authorship contribution statement

Mohammad Mahbubul Hassan: Writing – review & editing, Writing – original draft, Validation, Methodology, Data curation, Conceptualization. **Muhammad Naeem:** Writing – original draft, Data curation.

Declaration of competing interest

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

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Data availability

Data will be made available on request.

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