

Material Design and Mechanism Research for Photocatalytic Degradation of Organic Pollutants

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Abstract

Photocatalysis has emerged as an effective and sustainable approach for the degradation of organic pollutants, addressing global environmental concerns. This study explores the design and mechanisms of photocatalytic materials for efficient pollutant degradation. Traditional photocatalysts, such as TiO_2 and ZnO , exhibit high oxidative potential but suffer from limited visible-light absorption and charge recombination. To overcome these limitations, advanced photocatalytic materials, including narrow-bandgap semiconductors, carbon-based composites, metal-organic frameworks (MOFs), and heterostructured systems, have been extensively developed. Various modification strategies, such as element doping, heterojunction formation, and surface engineering, have further enhanced photocatalytic activity, stability, and pollutant selectivity. The mechanisms underlying photocatalytic degradation involve reactive oxygen species (ROS) generation and pollutant-specific degradation pathways, influenced by catalyst properties, light absorption, and reaction conditions. The study also examines the degradation of various organic pollutants, including industrial chemicals, pharmaceuticals, and environmental contaminants. By advancing material design and optimizing reaction parameters, this research contributes to the development of next-generation photocatalysts with improved efficiency and applicability in large-scale environmental remediation.

Keywords: *Photocatalysis; Organic Pollutants; Photocatalytic Materials; Degradation Mechanisms; Metal-Organic Frameworks; Reactive Oxygen Species; Surface Engineering*

1 INTRODUCTION

Organic pollution from dyes, pesticides, and pharmaceutical residues poses serious threats to ecosystems and human health due to their persistence and resistance to degradation. Traditional treatment methods often fall short, necessitating innovative solutions for pollutant removal. Photocatalysis has emerged as a promising approach, utilizing semiconductor materials under light irradiation to break down contaminants into less harmful byproducts. While materials like titanium dioxide (TiO_2) demonstrate high efficiency under UV light, their limited visible-light activity and high electron-hole recombination rates hinder performance. Recent research focuses on designing novel photocatalysts with enhanced stability, improved light absorption, and higher degradation efficiency. This study explores material design strategies and photocatalytic mechanisms to develop more effective and sustainable pollution control technologies. By optimizing photocatalytic systems, this research aims to advance next-generation environmental remediation solutions for large-scale applications.

2 MATERIALS FOR PHOTOCATALYTIC DEGRADATION

2.1 Traditional Photocatalytic Materials

Traditional photocatalytic materials have been extensively studied for their ability to degrade organic pollutants under light irradiation. Among these, titanium dioxide (TiO_2) is the most widely used semiconductor due to its strong oxidative ability, chemical stability, and non-toxicity. TiO_2 exists in three main crystalline forms: anatase, rutile, and brookite, with anatase exhibiting the highest photocatalytic efficiency due to its favorable band structure

and electron mobility. However, its wide bandgap (~ 3.2 eV for anatase) restricts its activation to ultraviolet (UV) light, which constitutes only a small fraction of the solar spectrum. This limitation has hindered its practical application in large-scale environmental remediation^[1].

Other traditional photocatalysts include zinc oxide (ZnO), which possesses a similar bandgap to TiO₂ but suffers from photocorrosion under irradiation, and cadmium sulfide (CdS), which has a narrower bandgap that allows visible light absorption but is prone to rapid photocorrosion and toxicity concerns. Despite their effectiveness under controlled laboratory conditions, these materials often exhibit limited efficiency and stability in real-world applications, necessitating further improvements to enhance their photocatalytic performance^[2].

2.2 Advanced Photocatalytic Materials

To overcome the limitations of traditional photocatalysts, significant research efforts have been devoted to developing advanced materials with improved optical absorption, charge separation, and stability. One such category includes narrow-bandgap semiconductors such as bismuth-based compounds (e.g., BiVO₄, Bi₂WO₆), which exhibit enhanced visible light absorption and catalytic activity. These materials possess unique layered structures that facilitate charge transfer and reduce electron-hole recombination.

Another promising class of photocatalysts is carbon-based materials, including graphene-based composites and graphitic carbon nitride (g-C₃N₄). Graphene enhances charge separation due to its high electrical conductivity and large surface area, while g-C₃N₄, with a bandgap of approximately 2.7 eV, can efficiently utilize visible light. Additionally, metal-organic frameworks (MOFs) have attracted considerable attention due to their tunable porosity, high surface area, and ability to incorporate metal centers that facilitate photocatalysis^[3].

Recently, heterostructured materials combining different semiconductors have gained interest due to their ability to form built-in electric fields, promoting charge separation. Examples include Z-scheme photocatalysts, which mimic natural photosynthesis by enabling effective charge carrier transfer, and plasmonic photocatalysts, which leverage localized surface plasmon resonance (LSPR) effects from noble metals such as gold (Au) and silver (Ag) to enhance light absorption and catalytic activity.

2.3 Modification Strategies for Enhancing Photocatalytic Properties

Given the inherent limitations of photocatalytic materials, various modification strategies have been explored to enhance their efficiency, stability, and selectivity. One widely used approach is element doping, where metal or non-metal atoms are introduced into the semiconductor lattice to tune the band structure and improve visible light absorption. For instance, nitrogen doping in TiO₂ has been shown to narrow its bandgap, allowing more efficient utilization of sunlight.

Heterojunction engineering is another effective strategy, where two or more semiconductors are combined to form an interface that promotes charge separation. Type-II heterojunctions, p-n junctions, and Z-scheme photocatalysts have been designed to optimize electron-hole migration and reduce recombination losses. Surface modification with co-catalysts, such as transition metal oxides and sulfides, can also enhance catalytic activity by facilitating charge transfer and providing additional reactive sites^[3].

Morphological control, including nanostructuring and surface engineering, has further improved photocatalyst performance. Nanostructured materials, such as nanorods, nanowires, and hollow nanospheres, exhibit higher surface areas and enhanced light-harvesting capabilities. Surface functionalization with hydrophilic or hydrophobic coatings can further tailor the interaction between the catalyst and pollutants, optimizing degradation efficiency.

3 MECHANISMS OF PHOTOCATALYTIC DEGRADATION

3.1 Reactive Oxygen Species (ROS) in Photocatalysis

The photocatalytic degradation of organic pollutants is primarily driven by the generation of reactive oxygen species (ROS), which play a crucial role in oxidative reactions. When a photocatalyst absorbs photons with energy equal to or greater than its bandgap, electrons in the valence band (VB) are excited to the conduction band (CB), leaving

behind holes in the VB. These charge carriers participate in redox reactions at the photocatalyst surface, leading to the formation of ROS such as hydroxyl radicals ($\bullet\text{OH}$), superoxide radicals ($\text{O}_2\bullet^-$), and singlet oxygen ($^1\text{O}_2$).

Hydroxyl radicals are the most potent oxidizing species in photocatalysis due to their high reactivity and ability to non-selectively degrade a wide range of organic contaminants. They are primarily generated through the oxidation of water molecules or hydroxide ions by photogenerated holes. Superoxide radicals are formed when conduction band electrons reduce molecular oxygen, which can further react to form hydrogen peroxide (H_2O_2) and hydroxyl radicals. Singlet oxygen, another key ROS, is produced through energy transfer processes and exhibits strong oxidative potential against organic compounds. The combined action of these ROS leads to the breakdown of complex organic pollutants into smaller intermediates and eventually into benign end products such as CO_2 and H_2O .

3.2 Degradation Pathways of Organic Pollutants

The photocatalytic degradation of organic pollutants follows a series of oxidative pathways that depend on the nature of the pollutant, the type of photocatalyst, and the reaction conditions. Generally, the process begins with the adsorption of pollutant molecules onto the photocatalyst surface, followed by their interaction with ROS or direct oxidation by photogenerated holes.

For aromatic compounds such as dyes and phenols, degradation typically involves hydroxylation, ring-opening, and subsequent mineralization. Hydroxyl radicals attack the aromatic rings, leading to the formation of hydroxylated intermediates, which undergo oxidative cleavage to form aliphatic carboxylic acids. These acids are further oxidized into smaller organic molecules and ultimately converted into CO_2 and H_2O .

For nitrogen-containing pollutants such as antibiotics and pesticides, degradation can involve demethylation, deamination, and oxidation of functional groups. Nitrogen-containing intermediates can be further transformed into ammonia, nitrate, or nitrogen gas, depending on reaction conditions. Similarly, for halogenated organic compounds, dehalogenation occurs as an initial step, followed by oxidative breakdown of the remaining hydrocarbon chains^[4].

The degradation pathways of organic pollutants can vary significantly depending on the photocatalyst and ROS involved. In some cases, partial degradation can lead to the formation of persistent or toxic intermediates, which may require extended treatment or additional catalytic modifications to ensure complete mineralization. Therefore, understanding degradation mechanisms is essential for optimizing photocatalytic systems for environmental remediation.

3.3 Influencing Factors in Photocatalytic Degradation

Several factors influence the efficiency of photocatalytic degradation, including the properties of the photocatalyst, the nature of the target pollutants, and the reaction conditions. One of the most critical parameters is light absorption, which determines the extent of photocatalyst activation. The wavelength, intensity, and duration of light exposure directly affect charge carrier generation and subsequent ROS formation. Visible-light-active photocatalysts have gained increasing attention due to their ability to utilize a broader portion of the solar spectrum, enhancing degradation efficiency.

Charge carrier dynamics play a crucial role in photocatalytic activity. Rapid recombination of photogenerated electrons and holes reduces the efficiency of ROS formation, limiting degradation performance. Strategies such as heterojunction formation, doping, and co-catalyst loading have been developed to suppress recombination and prolong charge carrier lifetimes.

The surface characteristics of photocatalysts, including surface area, porosity, and functional groups, significantly impact pollutant adsorption and reaction kinetics. High surface area materials provide more active sites for pollutant interaction, while surface modifications can improve selectivity and enhance ROS generation^[5].

Solution chemistry, including pH, dissolved oxygen concentration, and the presence of competing species, also affects degradation efficiency. The pH of the reaction medium influences the surface charge of the photocatalyst and the speciation of pollutants, thereby affecting adsorption and reactivity. Oxygen availability is crucial for ROS generation, particularly for superoxide and hydroxyl radical formation. Additionally, the presence of co-existing

organic or inorganic species may compete for ROS or act as scavengers, inhibiting photocatalytic degradation.

4 PHOTOCATALYTIC DEGRADATION OF DIFFERENT ORGANIC POLLUTANTS

4.1 Degradation of Hazardous Industrial Chemicals

Industrial activities release a wide range of hazardous organic chemicals into the environment, including dyes, phenols, and halogenated compounds. Many of these pollutants are highly persistent, toxic, and resistant to conventional wastewater treatment methods. Photocatalytic degradation has emerged as a promising approach for breaking down these hazardous chemicals into non-toxic byproducts.

Dyes, commonly used in the textile, leather, and paper industries, are among the most problematic industrial pollutants due to their synthetic nature and high stability. Traditional photocatalysts such as TiO_2 have demonstrated significant efficiency in degrading dye molecules through oxidative pathways involving hydroxyl radicals and direct electron transfer. The process typically begins with the cleavage of chromophoric groups, leading to the formation of smaller intermediates, which are further mineralized into CO_2 and H_2O . Advanced photocatalysts, including doped semiconductors and heterojunction materials, have been developed to enhance the visible-light response and improve degradation efficiency^[6].

Phenolic compounds, another major category of industrial pollutants, originate from petroleum refining, plastic manufacturing, and agrochemical industries. Due to their high toxicity and bioaccumulation potential, effective removal of phenols is critical for environmental safety. Photocatalytic oxidation of phenolic pollutants involves hydroxylation and subsequent cleavage of the benzene ring, eventually leading to the formation of biodegradable organic acids and complete mineralization. Modified photocatalysts with improved charge separation and surface functionalization have been explored to accelerate phenol degradation under mild reaction conditions.

Halogenated organic compounds, such as polychlorinated biphenyls (PCBs) and chlorinated solvents, pose additional challenges due to their chemical stability and potential for generating toxic intermediates. Photocatalytic degradation of these compounds often requires a combination of dehalogenation and oxidative cleavage. Studies have shown that metal-doped catalysts and composite photocatalysts with electron-rich active sites can enhance dechlorination efficiency, facilitating the breakdown of these hazardous chemicals into non-toxic end products.

4.2 Degradation of Pharmaceutical Contaminants

Pharmaceutical pollutants, including antibiotics, analgesics, hormones, and personal care products, have been increasingly detected in water bodies due to their widespread use and incomplete removal in conventional wastewater treatment plants. These contaminants pose serious environmental and health risks, including the development of antibiotic resistance and endocrine disruption. Photocatalytic degradation has emerged as an effective strategy for degrading pharmaceutical compounds, breaking them down into harmless substances^[7].

Antibiotics, such as tetracyclines, sulfonamides, and fluoroquinolones, are among the most concerning pharmaceutical contaminants due to their persistence and contribution to antimicrobial resistance. Photocatalytic oxidation of antibiotics involves hydroxylation, deamination, and cleavage of heterocyclic rings. The efficiency of degradation depends on factors such as catalyst properties, light source, and solution pH. Advanced photocatalysts, including graphene-based composites and metal-organic frameworks (MOFs), have demonstrated enhanced activity in decomposing antibiotics under visible light.

Hormonal pollutants, such as endocrine-disrupting compounds (EDCs) like bisphenol A (BPA) and synthetic estrogens, interfere with biological systems even at trace concentrations. Their degradation mechanisms involve hydroxyl radical attack, resulting in structural transformation and eventual mineralization. Photocatalytic processes utilizing nanostructured catalysts and plasmonic materials have been explored to accelerate the breakdown of EDCs and prevent their bioaccumulation.

Nonsteroidal anti-inflammatory drugs (NSAIDs), including ibuprofen, diclofenac, and naproxen, are frequently detected in wastewater due to high consumption rates. Photocatalytic degradation of these compounds proceeds

through oxidation of functional groups, leading to fragmentation into smaller intermediates. To improve degradation efficiency, researchers have focused on bandgap engineering and surface modification of photocatalysts to enhance charge separation and increase the generation of reactive oxygen species.

4.3 Degradation of Environmental Pollutants

In addition to industrial chemicals and pharmaceuticals, a wide range of organic pollutants, including pesticides, petroleum hydrocarbons, and microplastics, contribute to environmental contamination. Photocatalytic degradation offers a sustainable solution for breaking down these persistent pollutants into less harmful substances.

Pesticides, including herbicides, insecticides, and fungicides, are extensively used in agriculture but often persist in soil and water, causing ecological harm. Photocatalytic oxidation of pesticides involves hydroxylation, dechlorination, and fragmentation of molecular structures. Studies have demonstrated that visible-light-driven photocatalysts, such as BiVO_4 and g- C_3N_4 -based composites, exhibit enhanced degradation of organophosphates and chlorinated pesticides.

Petroleum hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs), originate from fossil fuel combustion, industrial spills, and vehicular emissions. These pollutants are known for their carcinogenic and mutagenic effects. Photocatalytic degradation of PAHs involves successive oxidation steps, converting them into less harmful organic acids and CO_2 . To enhance photocatalytic efficiency, researchers have explored nano-heterojunction materials and co-catalyst systems that promote charge carrier separation and extend light absorption into the visible range^[8].

Microplastics, a newly emerging category of environmental pollutants, pose severe threats to aquatic ecosystems and human health. Conventional degradation methods are ineffective in breaking down microplastics due to their polymeric nature and slow degradation kinetics. Recent studies have explored the potential of photocatalysis to fragment microplastics into smaller organic molecules through oxidation and chain scission reactions. Photocatalytic materials with enhanced surface reactivity and optimized band structures have been developed to accelerate microplastic degradation under sunlight-driven processes.

The application of photocatalysis in environmental remediation continues to expand, driven by advancements in material science and a deeper understanding of reaction mechanisms. By tailoring photocatalytic materials and optimizing reaction conditions, researchers aim to develop highly efficient and sustainable methods for eliminating diverse organic pollutants from the environment.

5 CONCLUSION

The development of efficient photocatalytic materials is crucial for addressing the challenges of organic pollutant degradation and environmental remediation. This study highlights the advancements in photocatalyst design, modification strategies, and degradation mechanisms, emphasizing their potential for real-world applications. While traditional materials such as TiO_2 and ZnO have demonstrated effectiveness, their limitations in visible-light utilization and charge recombination necessitate the development of advanced materials, including heterostructured semiconductors, carbon-based composites, and MOF-based systems. Understanding the role of reactive oxygen species and pollutant-specific degradation pathways further aids in optimizing photocatalytic efficiency. Future research should focus on enhancing the scalability, stability, and cost-effectiveness of photocatalysts while exploring innovative approaches such as hybrid photocatalysis and solar-driven systems. By integrating material science and environmental engineering, photocatalytic technology can play a pivotal role in achieving sustainable pollution control and environmental restoration.

REFERENCES

- [1] Patial B, Bansal A, Gupta R, et al. BiVO_4 -based heterojunction nanophotocatalysts for water splitting and organic pollutant degradation: a comprehensive review of photocatalytic innovation[J]. *Reviews in Inorganic Chemistry*, 2024, 44(4):495-519.

- [2] Xu Q, Sun F, Liu X, et al. Upconverting luminescence and surface plasmon resonance synergistically boost photocatalytic activity of LaOCl:Yb³⁺,Er³⁺/Bi₂MoO₆/Ag nanofiber S-scheme heterojunction photocatalyst for degradation of organic contaminants[J]. Journal of Alloys and Compounds,2025,1020179363-179363.
- [3] Li X, Yang R, Zou L, et al. Reassessing the Role of Thermal Convection in Simultaneous Water Production and Pollutant Degradation in Interfacial Photothermal-Photocatalytic Systems.[J]. Advanced materials (Deerfield Beach, Fla.),2024,37(4):e2416283.
- [4] Xiao L, Wang Y, Yan J, et al. Enhanced BiVO₄ photocatalyst anchored on construction waste bricks powder for efficient formaldehyde and methylene blue degradation[J]. Construction and Building Materials,2025,469140536-140536.
- [5] Li Z, Su P, Wang A, et al. Sequential anaerobic-aerobic photocatalytic degradation of halogenated organic pollutants via dual-site confined carbon nitride[J]. Journal of Hazardous Materials,2025,490137861-137861.
- [6] Li Y, Song J, Yang J, et al. A novel S-scheme heterojunction based on BiPO₄/CdPSe₃ for effective photocatalytic degradation of organic pollutants[J]. Journal of Alloys and Compounds,2025,1010177491-177491.
- [7] Mohamed H H, Alqahtani S, Alsunaidi H Z .Sulphur doped boron carbon nitride as novel metal free nanomaterials for photocatalytic degradation of organic pollutants and H₂ production[J]. Journal of Alloys and Compounds,2025,1018179236-179236.
- [8] Kumari R, Kumar R .Enhanced photocatalytic degradation of organic pollutants by randomly oriented 2D SnS₂ nanostructures[J]. Semiconductor Science and Technology,2024,39(12):125003-125003.