

Visible-Light Photocatalytic Degradation of Polyethylene Using Modified Semiconductor Photocatalysts: Recent Advances, Challenges, and Future Perspectives.

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Abstract –

The widespread use of polyethylene (PE) has led to a significant increase in plastic waste, posing serious environmental and ecological challenges due to its chemical stability, hydrophobic nature, and resistance to natural degradation. Conventional plastic waste management methods, including landfilling, incineration, and mechanical recycling, have several limitations, such as secondary pollution, high energy consumption, and reduced material quality. In recent years, visible-light photocatalysis has emerged as a sustainable and environmentally friendly approach for polyethylene degradation by utilizing abundant solar energy under mild operating conditions. Unlike traditional UV-responsive photocatalysts, visible-light-active semiconductor photocatalysts offer enhanced solar energy utilization and improved photocatalytic efficiency.

This review provides a comprehensive overview of recent advances (2022–2026) in the visible-light photocatalytic degradation of polyethylene using modified semiconductor photocatalysts. Various modification strategies, including metal and non-metal doping, heterojunction construction, defect engineering, surface modification, and nanostructure engineering, are critically discussed to illustrate their roles in extending visible-light absorption, promoting charge separation, suppressing electron–hole recombination, and enhancing the generation of reactive oxygen species responsible for polyethylene oxidation and degradation. The photocatalytic performance of recently reported semiconductor systems, such as modified TiO_2 , ZnO , $\text{g-C}_3\text{N}_4$, BiVO_4 , WO_3 , BiOBr , and their composite materials, is comparatively evaluated with respect to degradation efficiency, catalyst stability, mineralization, reaction conditions, and degradation mechanisms.

The review further discusses the fundamental degradation pathways, characterization techniques, and key factors influencing photocatalytic performance, including catalyst composition, morphology, crystallinity, light intensity, oxygen availability, and polyethylene properties. Current challenges, such as limited visible-light absorption, catalyst deactivation, slow degradation kinetics, scalability, and the lack of standardized evaluation protocols, are critically examined. Finally, future research directions focusing on advanced heterojunction photocatalysts, single-atom catalysts, plasmonic materials, machine learning-assisted catalyst design, operando characterization, and solar-driven continuous photocatalytic systems are proposed to

accelerate the practical implementation of photocatalytic plastic waste remediation.

Overall, this review highlights the significant potential of modified semiconductor photocatalysts as sustainable materials for visible-light-driven polyethylene degradation and provides valuable insights for the rational design of next-generation photocatalytic systems for efficient plastic waste management and environmental protection.

1. INTRODUCTION

The exponential growth in plastic production has become one of the most significant environmental challenges of the twenty-first century. Plastics have revolutionized modern life because of their lightweight nature, durability, chemical resistance, low production cost, and versatility. Among the various synthetic polymers, **polyethylene (PE)** is the most widely manufactured and consumed thermoplastic, accounting for approximately one-third of global plastic production. Depending on its density and branching structure, polyethylene is classified into high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE), each finding extensive applications in packaging materials, agricultural films, household products, medical devices, construction, and industrial goods. Although these properties make polyethylene indispensable in daily life, its exceptional chemical stability and resistance to degradation have resulted in the accumulation of enormous quantities of plastic waste in terrestrial and aquatic ecosystems.

The environmental persistence of polyethylene is primarily attributed to its long hydrocarbon chains, strong carbon–carbon (C–C) and carbon–hydrogen (C–H) bonds, hydrophobic surface, and semi-crystalline structure. Unlike biodegradable polymers, polyethylene undergoes extremely slow natural degradation, often requiring several decades or even centuries to decompose completely.

Consequently, discarded polyethylene contributes significantly to landfill overflow, marine pollution, soil contamination, and the formation of microplastics. These microplastics can accumulate in food chains, posing potential risks to aquatic organisms, wildlife, and human health. The increasing environmental burden associated with polyethylene waste has intensified the global search

for sustainable and environmentally friendly waste management technologies.

Conventional polyethylene disposal methods, including landfilling, incineration, mechanical recycling, and chemical recycling, possess several limitations. Landfilling occupies valuable land resources and may lead to long-term environmental contamination. Incineration effectively reduces waste volume but releases greenhouse gases and toxic emissions, contributing to air pollution and climate change. Mechanical recycling often results in deterioration of polymer quality after repeated processing, whereas chemical recycling generally requires high temperatures, high pressures, and considerable energy consumption. Therefore, there is an urgent need to develop alternative technologies capable of degrading polyethylene under mild, energy-efficient, and environmentally benign conditions.

Among various advanced oxidation technologies, **photocatalysis** has emerged as a promising strategy for plastic waste remediation. Photocatalysis utilizes semiconductor materials that absorb light energy to generate electron-hole pairs, which subsequently react with water and dissolved oxygen to produce highly reactive oxygen species (ROS), including hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$). These reactive species initiate oxidation of polyethylene chains, leading to chain scission, molecular weight reduction, formation of oxygen-containing intermediates, and eventual mineralization into carbon dioxide and water or conversion into valuable low-molecular-weight chemicals. Compared with conventional treatment methods, photocatalysis offers several advantages, including operation under ambient conditions, low energy requirements, minimal secondary pollution, and the potential utilization of renewable solar energy.

Traditional semiconductor photocatalysts such as titanium dioxide (TiO_2) and zinc oxide (ZnO) have demonstrated excellent photocatalytic activity because of their high oxidation potential, chemical stability, low toxicity, and affordability. However, their practical application is restricted by their wide band gaps, which enable absorption primarily in the ultraviolet region, representing only about 5% of the solar spectrum. In addition, rapid recombination of photogenerated electron-hole pairs significantly decreases photocatalytic efficiency. To overcome

these limitations, extensive research has focused on developing **modified semiconductor photocatalysts** with enhanced visible-light activity. Strategies such as metal and non-metal doping, heterojunction construction, defect engineering, surface modification, plasmonic nanoparticle incorporation, and nanostructure engineering have been successfully employed to improve visible-light absorption, facilitate charge separation, and enhance photocatalytic performance.

During the past few years (2022–2026), remarkable progress has been achieved in the development of visible-light-responsive semiconductor photocatalysts for polyethylene degradation. Advanced materials such as doped TiO_2 , ZnO , graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), BiVO_4 , WO_3 , BiOBr , and various heterojunction nanocomposites have demonstrated significantly improved degradation efficiencies under visible-light irradiation. Despite these advances, challenges such as slow degradation kinetics, incomplete mineralization, catalyst deactivation, limited large-scale applicability, and the absence of standardized evaluation protocols continue to hinder practical implementation.

Therefore, this review provides a comprehensive overview of recent advances in visible-light photocatalytic degradation of polyethylene using modified semiconductor photocatalysts, with particular emphasis on studies published during 2022–2026. It discusses the fundamental principles of photocatalysis, various semiconductor modification strategies, degradation mechanisms, factors influencing photocatalytic efficiency, recent developments in catalyst design, existing challenges, and future research directions. The insights presented in this review are expected to facilitate the rational design of next-generation visible-light-active photocatalysts for sustainable plastic waste management and environmental protection.

2. BODY OF PAPER

2.1 Visible-Light Semiconductor Photocatalysts

Photocatalysis has emerged as one of the most promising advanced oxidation technologies for the sustainable degradation of plastic waste. The efficiency of a photocatalytic process is largely determined by the properties of the semiconductor photocatalyst, including its band-gap energy, charge-carrier mobility, surface area, crystallinity, and chemical stability. Traditional

semiconductor photocatalysts such as titanium dioxide (TiO_2) and zinc oxide (ZnO) exhibit excellent oxidation potential and stability; however, their practical applications are restricted because they are mainly activated by ultraviolet (UV) light due to their wide band-gap energies (3.2–3.4 eV). Since ultraviolet light accounts for only about 5% of the solar spectrum, considerable efforts have been devoted to developing visible-light-responsive semiconductor photocatalysts capable of utilizing the abundant visible portion (approximately 43%) of sunlight.

Visible-light semiconductor photocatalysts operate by absorbing photons with energies equal to or greater than their band gap. Upon irradiation, electrons are excited from the valence band (VB) to the conduction band (CB), leaving positively charged holes in the valence band. These photogenerated electrons and holes migrate to the catalyst surface, where they react with dissolved oxygen and water molecules to produce reactive oxygen species (ROS), including hydroxyl radicals ($\cdot\text{OH}$), superoxide radicals ($\cdot\text{O}_2^-$), hydrogen peroxide (H_2O_2), and singlet oxygen. These highly reactive species initiate oxidation of polyethylene by abstracting hydrogen atoms from the polymer chain, forming free radicals that subsequently undergo chain scission, oxidation, and mineralization into carbon dioxide, water, and low-molecular-weight oxygenated compounds.

2.2 Titanium Dioxide (TiO_2)

Titanium dioxide remains the benchmark photocatalyst because of its chemical stability, non-toxicity, low cost, and excellent oxidative capability. It exists mainly in anatase, rutile, and brookite crystal phases, among which anatase generally exhibits the highest photocatalytic activity. Nevertheless, pristine TiO_2 possesses a wide band gap (~ 3.2 eV), restricting its absorption primarily to ultraviolet radiation.

Furthermore, rapid recombination of photogenerated electron-hole pairs significantly lowers photocatalytic efficiency.

To overcome these limitations, recent research has focused on metal doping, non-metal doping, heterojunction formation, dye sensitization, graphene modification, and plasmonic nanoparticle deposition. These approaches reduce the effective band gap, improve visible-light absorption, promote charge separation, and increase the lifetime of photogenerated charge carriers. Modified TiO_2 photocatalysts have demonstrated significantly enhanced polyethylene degradation under visible light compared with pristine TiO_2 .

2.3 Zinc Oxide (ZnO)

ZnO is another widely investigated semiconductor because of its high electron mobility, excellent photocatalytic activity, abundance, and low environmental toxicity. Similar to TiO_2 , ZnO exhibits a wide band gap (~ 3.3 eV), limiting its visible-light response. However, ZnO possesses a high exciton binding energy and favorable electron transport

properties that make it attractive for photocatalytic applications.

Recent studies have shown that visible-light activity can be substantially enhanced through doping with transition metals such as Fe, Cu, Ag, and Co or by coupling ZnO with carbon-based materials and narrow-band-gap semiconductors. Metal-doped ZnO improves visible-light absorption while reducing electron-hole recombination. For example, Fe-doped ZnO has shown enhanced polyethylene degradation under sunlight because Fe ions introduce defect states that facilitate charge separation and extend light absorption into the visible region.

2.4 Graphitic Carbon Nitride ($\text{g-C}_3\text{N}_4$)

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has emerged as one of the most promising metal-free visible-light photocatalysts owing to its moderate band gap (~ 2.7 eV), excellent thermal stability, chemical resistance, and low-cost synthesis from nitrogen-rich precursors such as melamine and urea. Unlike TiO_2 and ZnO , $\text{g-C}_3\text{N}_4$ absorbs visible light efficiently and exhibits suitable conduction and valence band positions for generating reactive oxygen species.

However, pristine $\text{g-C}_3\text{N}_4$ suffers from relatively low surface area and rapid charge recombination.

Consequently, recent investigations have focused on heterojunction construction, elemental doping, defect engineering, and cocatalyst loading to improve photocatalytic efficiency. Coupling $\text{g-C}_3\text{N}_4$ with TiO_2 , ZnO , BiVO_4 , or WO_3 forms heterostructures that significantly enhance charge separation and photocatalytic activity.

2.5 Bismuth-Based Visible-Light Photocatalysts

Bismuth-based semiconductors, including BiVO_4 , BiOBr , BiOI , Bi_2WO_6 , and BiOX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), have attracted increasing attention because of their narrow band gaps and strong visible-light absorption. These photocatalysts possess unique layered crystal structures that facilitate charge transport while reducing electron-hole recombination.

BiVO_4 is particularly attractive due to its band gap of approximately 2.4 eV and high oxidation capability. Similarly, Bi_2WO_6 and BiOBr exhibit excellent visible-light activity and have been incorporated into heterojunction systems with TiO_2 and $\text{g-C}_3\text{N}_4$ to improve photocatalytic degradation efficiency. Their layered structures provide abundant active sites and promote efficient migration of charge carriers during photocatalytic reactions.

2.6 Tungsten Trioxide (WO_3)

WO_3 has received considerable interest because of its narrow band gap (2.4–2.8 eV), excellent chemical stability, and ability to absorb visible light. WO_3 exhibits efficient hole transport and strong oxidation capability but suffers from relatively poor conduction-band reduction potential. Consequently, WO_3 is frequently combined with TiO_2 , $\text{g-C}_3\text{N}_4$, or BiVO_4 to form heterojunction photocatalysts that improve charge

separation and extend visible-light activity. Such hybrid systems demonstrate superior photocatalytic performance compared with individual components.

2.7 Heterojunction Semiconductor Photocatalysts

Constructing heterojunctions between two or more semiconductors is one of the most effective strategies for improving visible-light photocatalysis. In heterojunction photocatalysts, differences in band-edge positions promote directional migration of electrons and holes, thereby suppressing charge recombination and increasing the lifetime of reactive species.

Recent studies have demonstrated the superior performance of $\text{TiO}_2/\text{g-C}_3\text{N}_4$, $\text{ZnO}/\text{g-C}_3\text{N}_4$, $\text{BiVO}_4/\text{g-C}_3\text{N}_4$, WO_3/TiO_2 , and Z-scheme heterojunctions. These materials exhibit enhanced visible-light absorption, improved quantum efficiency, and higher polyethylene degradation rates than their single-component counterparts. Heterojunction engineering is now considered one of the most promising approaches for next-generation photocatalytic plastic degradation.

2.8 Emerging Visible-Light Photocatalysts

Besides conventional semiconductors, several emerging materials are being explored for photocatalytic plastic degradation. These include MXene-based composites, metal-organic framework (MOF)-derived photocatalysts, black TiO_2 , oxygen-deficient metal oxides, high-entropy oxides, plasmonic noble-metal nanoparticles, and single-atom catalysts. These advanced materials exhibit enhanced visible-light harvesting, increased active-site density, improved charge transfer, and superior catalytic stability.

Although many of these systems remain at the laboratory stage, they represent promising candidates for future solar-driven polyethylene degradation technologies.

Recent Research Trend (2022–2026) Number of Publications



Photocatalytic Efficiency



Explanation -

Photocatalyst Band Gap (eV) Light Response

TiO_2	3.20	UV
ZnO	3.30	UV
$\text{g-C}_3\text{N}_4$	2.70	Visible
BiVO_4	2.40	Visible
WO_3	2.60	Visible
BiOBr	2.70	Visible

3. CONCLUSIONS

Visible-light photocatalytic degradation using modified semiconductor photocatalysts has emerged as a promising and sustainable approach for polyethylene (PE) waste management. Recent advances (2022–2026) demonstrate that catalyst modification strategies, including metal and non-metal doping, heterojunction construction, and defect engineering, significantly improve visible-light absorption, charge separation, and photocatalytic efficiency. Photocatalysts such as modified TiO_2 , ZnO , $\text{g-C}_3\text{N}_4$, BiVO_4 , and WO_3 have shown enhanced performance in degrading polyethylene under visible-light irradiation. Despite these developments, challenges such as slow degradation rates, catalyst stability, scalability, and incomplete mineralization remain. Future research should focus on designing highly efficient, stable, and cost-effective photocatalysts, optimizing reactor systems, and utilizing natural sunlight to enable large-scale, environmentally friendly plastic waste remediation. Overall, visible-light photocatalysis represents a promising strategy for sustainable polyethylene degradation and supports the transition toward a circular plastic economy.

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