
Comparative Photocatalytic Performance of Graphene-Modified Titanium Dioxide and Zinc Oxide Nanostructures for Solar-Driven Wastewater Remediation

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ABSTRACT

Increasing industrialization and urban wastewater discharge have intensified the global presence of persistent organic pollutants, pharmaceutical residues, dyes, and heavy-metal-associated contaminants within aquatic systems. Semiconductor photocatalysis has emerged as a promising sustainable remediation strategy because it enables solar-driven degradation of toxic compounds through advanced oxidation mechanisms. This study comparatively analyzes the photocatalytic performance of graphene-modified titanium dioxide (G–TiO₂) and graphene-modified zinc oxide (G–ZnO) nanostructures for wastewater remediation under simulated solar irradiation. The article investigates how structural modification, electron-transfer dynamics, band-gap characteristics, reactive oxygen species generation, and physicochemical stability influence measurable remediation efficiency and environmental sustainability. Using comparative materials analysis, spectroscopy-based characterization evidence, computational interpretation, and peer-reviewed experimental literature, the study evaluates the mechanistic differences between TiO₂- and ZnO-based photocatalytic systems. The findings indicate that graphene incorporation substantially improves charge separation efficiency, surface adsorption capacity, and visible-light responsiveness in both systems. However, G–TiO₂ demonstrates greater long-term physicochemical stability and photocorrosion resistance, whereas G–ZnO exhibits higher short-term electron mobility and rapid degradation kinetics under optimized conditions. The comparative evidence further reveals that photocatalytic efficiency depends not solely on semiconductor composition but

specific reaction pathways. This article contributes to natural sciences scholarship by integrating nanomaterials science, environmental chemistry, photocatalytic physics, and sustainability-oriented engineering into a unified framework explaining solar-driven pollutant degradation mechanisms and technological scalability for environmental remediation systems.

Keywords: photocatalysis; graphene nanocomposites; titanium dioxide; zinc oxide; wastewater remediation; nanomaterials; solar energy; advanced oxidation; environmental chemistry; sustainable technology

INTRODUCTION

The rapid expansion of industrial manufacturing, pharmaceutical consumption, textile processing, agricultural intensification, and urbanization has significantly increased the release of persistent contaminants into aquatic environments. Industrial dyes, antibiotics, endocrine-disrupting compounds, pesticides, and heavy-metal-associated organics are increasingly detected in rivers, lakes, groundwater systems, and coastal ecosystems, generating ecological toxicity and public health risks (WHO, 2024; UNEP, 2025). Conventional wastewater treatment systems frequently demonstrate limited efficiency in removing chemically stable micropollutants because many contaminants resist biological degradation and remain persistent under standard treatment conditions (Ahmed et al., 2020).

This environmental challenge has intensified scientific interest in advanced oxidation processes and semiconductor photocatalysis. Photocatalytic systems utilize light-driven excitation of semiconductor materials to generate reactive oxygen species capable of degrading organic contaminants into less toxic or mineralized products (Fujishima et al., 2008). Under irradiation exceeding the semiconductor band-gap energy, electron–hole pairs are generated, enabling oxidative and reductive reactions involving hydroxyl radicals, superoxide radicals, and dissolved oxygen species. Consequently, photocatalysis represents a potentially sustainable environmental remediation strategy because it may utilize solar energy rather than chemically intensive treatment systems.

Titanium dioxide (TiO₂) and zinc oxide (ZnO) remain among the most extensively studied photocatalytic semiconductors because of their low toxicity, relatively low cost, high catalytic potential, and physicochemical versatility (Chen et al., 2020; Kumar & Rao, 2021). TiO₂ demonstrates strong chemical stability, oxidative capability, and corrosion resistance, while ZnO exhibits high electron mobility and strong ultraviolet absorption efficiency. Nevertheless, both materials possess important limitations, including rapid electron–hole recombination, restricted visible-light absorption, photocorrosion susceptibility, and limited charge-transfer efficiency under practical environmental conditions.

Nanostructure engineering and carbon-based modifications have emerged as major strategies for overcoming these limitations. Graphene and graphene-derived materials possess high electrical conductivity, exceptional surface area, electron transport capability, and mechanical stability, making them attractive for semiconductor modification (Geim & Novoselov, 2007). The integration of graphene into semiconductor

photocatalysts may enhance adsorption capacity, suppress charge recombination, improve electron transport pathways, and extend photoresponse into broader spectral regions.

Recent studies indicate that graphene-modified photocatalysts exhibit significantly improved degradation efficiency against dyes, pharmaceuticals, and organic pollutants (Zhang et al., 2021; Li et al., 2022). However, current natural sciences literature remains fragmented in explaining how graphene modifies TiO₂ and ZnO differently at the physicochemical and electronic levels. While previous studies emphasize photocatalytic efficiency metrics, other researchers argue that long-term material stability, electron-transfer mechanisms, oxygen-vacancy dynamics, and scalability constraints are equally important for environmental application.

Several major research gaps remain unresolved. First, comparative analysis between graphene-modified TiO₂ and graphene-modified ZnO under environmentally relevant conditions remains limited. Second, existing scholarship often prioritizes degradation percentages without sufficiently analyzing mechanistic differences in charge separation, photocorrosion, and interfacial electron transport. Third, photocatalytic studies frequently focus on laboratory-scale pollutant degradation without integrating broader sustainability implications such as material stability, scalability, and environmental compatibility. Fourth, current literature insufficiently explains how nanoscale structural differences influence radical generation pathways and contaminant-specific degradation mechanisms.

This article addresses these limitations through an interdisciplinary comparative analysis integrating materials science, environmental chemistry, nanotechnology, photocatalytic physics, and sustainability science. The study argues that photocatalytic efficiency is fundamentally governed by the interaction between semiconductor structure, graphene-mediated charge transfer, surface adsorption behavior, oxygen vacancy formation, and photochemical radical dynamics. Consequently, photocatalytic performance should not be interpreted merely through degradation percentages but through broader physicochemical and environmental mechanisms.

The novelty of this article lies in its comparative mechanistic interpretation of graphene-modified TiO₂ and ZnO systems within a sustainability-oriented environmental remediation framework. Unlike previous studies emphasizing isolated photocatalytic metrics, this article comparatively evaluates charge-transfer dynamics, crystallographic behavior, photocorrosion resistance, adsorption mechanisms, and scalability implications.

The analytical framework developed in this study follows the causal sequence: material composition → electronic and structural modification → reactive oxygen species generation → photocatalytic degradation efficiency → environmental remediation outcomes. Graphene integration modifies semiconductor behavior through enhanced electron mobility, reduced recombination probability, improved adsorption interactions, and altered surface chemistry. These physicochemical changes influence measurable remediation outcomes including degradation kinetics, mineralization efficiency, and operational stability.

This study therefore aims to analyze comparatively how graphene-modified TiO₂ and graphene-modified ZnO nanostructures influence photocatalytic efficiency, physicochemical stability, charge-transfer dynamics, and environmental remediation performance within solar-driven wastewater treatment systems.

METHODOLOGY

This study employs a comparative interdisciplinary materials-science research design integrating photocatalytic mechanism analysis, semiconductor nanostructure evaluation, environmental chemistry interpretation, and sustainability-oriented technological assessment to examine how graphene modification influences the photocatalytic performance of TiO₂ and ZnO systems. Graphene-modified titanium dioxide (G-TiO₂) and graphene-modified zinc oxide (G-ZnO) were selected because they represent two of the most widely investigated semiconductor photocatalytic architectures with distinct electronic, crystallographic, and physicochemical characteristics. The comparative framework aligns semiconductor physics, nanomaterials engineering, and environmental remediation theory by examining how graphene incorporation alters charge-transfer dynamics, band-gap interactions, electron-hole recombination behavior, adsorption capacity, photocorrosion resistance, oxygen-vacancy formation, and reactive oxygen species generation. The unit of analysis consists of photocatalytic nanostructure systems under solar or simulated solar irradiation. Analytical variables include crystallographic structure, band-gap energy, graphene loading behavior, surface area characteristics, electron mobility, radical generation efficiency, contaminant degradation kinetics, physicochemical stability, and photocatalytic reusability under repeated operational conditions.

The empirical foundation is derived from peer-reviewed experimental photocatalysis studies, spectroscopy-based characterization evidence, electron microscopy analyses, X-ray diffraction datasets, photoluminescence investigations, electrochemical impedance interpretations, computational semiconductor analyses, and environmental remediation literature published between 2020 and 2026. Comparative interpretation focused on mechanistic relationships between semiconductor composition and measurable remediation outcomes rather than fabrication of new laboratory measurements. Analytical triangulation was achieved by cross-comparing convergent findings from photocatalytic degradation studies, materials characterization research, and theoretical semiconductor modeling. Mechanistic evaluation prioritized experimentally validated pathways involving electron-transfer suppression, graphene-mediated conductivity enhancement, hydroxyl radical generation, photocorrosion inhibition, and contaminant mineralization efficiency. Validation and reproducibility considerations were addressed through emphasis on repeatedly observed trends across independent studies and standardized characterization approaches. Ethical and environmental considerations were incorporated by evaluating sustainability dimensions including material toxicity, solar energy utilization, catalyst reusability, and long-term environmental compatibility. Although the study relies on comparative synthesis rather than original experimental fabrication, the design provides analytically robust insight into semiconductor nanostructure optimization for environmentally sustainable wastewater remediation systems.

Findings and Discussion

1. Semiconductor Structure, Band-Gap Characteristics, and Electron Dynamics

The comparative evidence demonstrates that photocatalytic performance is fundamentally governed by semiconductor electronic structure, charge-transfer dynamics, and interfacial interactions between graphene and the host semiconductor material. TiO₂ and ZnO possess similar wide band-gap energies within the ultraviolet spectral range, yet they exhibit substantially different electron mobility, surface chemistry, and physicochemical stability profiles.

TiO₂, particularly in anatase crystalline form, demonstrates high oxidative potential and strong physicochemical stability. However, its large band-gap energy restricts visible-light utilization and contributes to rapid electron–hole recombination under irradiation. Graphene incorporation modifies this limitation by functioning as an electron-accepting conductive network that facilitates interfacial charge separation. Electron transfer from excited TiO₂ conduction bands toward graphene sheets reduces recombination probability and increases radical generation efficiency (Chen et al., 2020).

ZnO demonstrates comparatively higher electron mobility and rapid photoresponse capability due to its electronic structure and defect-mediated conductivity. Nevertheless, ZnO systems are more susceptible to photocorrosion and dissolution under prolonged irradiation and acidic conditions. Graphene integration substantially improves ZnO electron transport behavior by enhancing conductivity pathways and stabilizing electron migration across semiconductor interfaces (Kumar & Rao, 2021).

The comparative evidence reveals that graphene does not function merely as a passive support material. Rather, it modifies semiconductor energy landscapes through electron delocalization, surface adsorption enhancement, and nanoscale interfacial interactions. These modifications influence measurable photocatalytic outcomes including contaminant degradation kinetics, quantum efficiency, and catalyst stability.

Cross-system comparison indicates that G–ZnO often demonstrates superior short-term photocatalytic kinetics because rapid electron transport enhances radical generation rates under optimized conditions. However, G–TiO₂ generally demonstrates stronger long-term operational stability and resistance to photocorrosion. This distinction is environmentally significant because remediation technologies require both catalytic efficiency and sustained physicochemical integrity.

These findings support previous semiconductor photocatalysis research emphasizing the importance of electron–hole separation in determining catalytic performance (Fujishima et al., 2008). However, this article extends existing scholarship by comparatively interpreting graphene-mediated interfacial mechanisms rather than evaluating degradation percentages alone.

Scientifically, the findings suggest that future photocatalyst design should prioritize nanoscale interface engineering rather than simple compositional modification. Environmentally, stable long-term

photocatalytic functionality is essential for sustainable wastewater remediation deployment.

2. Reactive Oxygen Species Generation and Pollutant Degradation Mechanisms

Reactive oxygen species generation constitutes the central mechanistic process underlying semiconductor photocatalysis. Under irradiation, excited electrons and holes interact with dissolved oxygen and water molecules to generate hydroxyl radicals, superoxide radicals, and oxidative intermediates capable of degrading organic contaminants into smaller and potentially mineralized products.

In G–TiO₂ systems, graphene-mediated electron extraction enhances hydroxyl radical production by reducing recombination losses. Hydroxyl radicals possess extremely high oxidation potential and are particularly effective against dye molecules, aromatic hydrocarbons, and pharmaceutical contaminants. TiO₂ surfaces also demonstrate strong adsorption compatibility with hydroxylated compounds and oxygenated intermediates, improving catalytic interaction efficiency.

G–ZnO systems exhibit stronger initial superoxide radical generation under optimized irradiation because rapid electron transfer enhances oxygen reduction pathways. This may produce faster degradation rates for some contaminants, especially dyes and electron-rich aromatic compounds. However, ZnO photocorrosion can reduce long-term radical generation consistency under repeated operational cycles.

Experimental literature indicates that graphene incorporation significantly improves adsorption capability in both systems because graphene surfaces possess high specific surface area and π -electron interactions with aromatic pollutants (Li et al., 2022). This adsorption enhancement is environmentally important because photocatalytic efficiency depends not only on radical production but also on pollutant accessibility to reactive sites.

Table 1. Comparative Matrix of Experimental Variables, Scientific Mechanisms, and Measurable Outcomes

Variable	Case/System 1: G–TiO ₂	Case/System 2: G–ZnO	Empirical Evidence	Analytical Interpretation
Semiconductor stability	High physicochemical stability	Higher photocorrosion susceptibility	Repeated-cycle photocatalytic studies	Stability influences long-term remediation sustainability
Electron mobility	Moderate conductivity improved by graphene	High intrinsic electron mobility enhanced further by graphene	Electrochemical impedance and photoluminescence studies	Charge-transfer efficiency governs radical generation

Reactive oxygen species dominance	Strong hydroxyl radical generation	Enhanced superoxide radical pathways	Radical scavenging and degradation analyses	Different radical mechanisms influence contaminant specificity
Band-gap characteristics	UV-active with improved visible response after graphene integration	Similar UV range but faster electron transfer dynamics	Spectroscopy and optical absorption studies	Graphene alters electronic response behavior
Adsorption capability	Enhanced through graphene-supported surface interactions	Strong adsorption but influenced by ZnO surface instability	Surface area and adsorption studies	Adsorption mediates photocatalytic accessibility
Degradation kinetics	Slower initial kinetics but higher stability	Faster short-term degradation rates	Dye and pharmaceutical degradation experiments	Efficiency must be interpreted temporally
Environmental scalability	Strong long-term operational suitability	Higher efficiency under controlled conditions but lower durability	Reusability and photocorrosion evidence	Sustainability depends on operational resilience
Sustainability implications	Better for prolonged treatment systems	Potentially useful for rapid remediation applications	Comparative remediation analyses	Different systems suit different environmental conditions

The comparative matrix demonstrates that photocatalytic performance cannot be evaluated through degradation percentages alone. G–ZnO systems may outperform G–TiO₂ in short-duration degradation experiments, yet long-term photocorrosion and structural instability may reduce operational sustainability. Conversely, G–TiO₂ systems may exhibit slower kinetics but stronger long-term functionality and environmental compatibility.

Analytically, this indicates that photocatalytic optimization depends on matching semiconductor characteristics with environmental application requirements. Rapid emergency remediation may prioritize electron-transfer kinetics, whereas continuous wastewater treatment systems require physicochemical durability and catalytic stability.

The findings extend environmental photocatalysis scholarship by integrating radical chemistry, semiconductor physics, and sustainability-oriented interpretation into a comparative framework. Existing literature often treats photocatalytic efficiency as a singular parameter rather than a multidimensional systems property.

3. Surface Chemistry, Oxygen Vacancies, and Nanostructure Interactions

Surface chemistry and oxygen-vacancy dynamics play critical roles in determining photocatalytic functionality. Oxygen vacancies act as electron-trapping sites that may either improve charge separation or promote recombination depending on concentration, distribution, and semiconductor structure.

In G–TiO₂ systems, graphene interfaces stabilize electron-transfer pathways and may facilitate oxygen-vacancy-mediated conductivity enhancement without severe structural degradation. This contributes to stronger long-term photocatalytic consistency under repeated irradiation cycles. X-ray photoelectron spectroscopy and electron microscopy studies indicate that graphene incorporation also alters surface hydroxylation behavior, improving pollutant adsorption and radical accessibility.

In G–ZnO systems, oxygen vacancies can significantly enhance visible-light absorption and conductivity. However, excessive vacancy formation may destabilize lattice integrity and accelerate photocorrosion. This reflects an important physicochemical trade-off between catalytic activity and material durability.

The comparative evidence reveals that graphene functions as both an electronic and structural modifier. Electronically, it improves conductivity and suppresses recombination. Structurally, it influences nanoscale particle dispersion, aggregation resistance, and interfacial stability. Consequently, photocatalytic outcomes emerge from integrated nanoscale interactions rather than isolated material properties.

These findings align with nanomaterials theory emphasizing interface-controlled functionality in semiconductor composites (Geim & Novoselov, 2007). However, this article extends existing scholarship by demonstrating that oxygen-vacancy optimization must be interpreted dynamically rather than statically. Vacancy concentration beneficial under one irradiation regime may become destabilizing under prolonged environmental exposure.

The environmental implication is that sustainable photocatalytic systems require balance between activity enhancement and structural resilience. Highly reactive systems may not be environmentally optimal if degradation products, catalyst instability, or photocorrosion reduce operational lifespan.

Managerially and technologically, scalable photocatalytic deployment therefore requires integrated design approaches combining nanoscale engineering, reactor optimization, contaminant-specific analysis, and lifecycle sustainability evaluation.

4. Comparative Environmental Applications and Sustainability Implications

The comparative findings indicate that graphene-modified photocatalysts possess substantial potential for sustainable wastewater remediation, particularly in addressing persistent organic contaminants resistant to biological treatment systems. However, environmental scalability depends on more than laboratory degradation efficiency.

G-TiO₂ systems are particularly promising for long-term treatment infrastructures because of their chemical durability, resistance to photodegradation, and compatibility with repeated operational cycles. These properties make TiO₂-based systems attractive for solar-driven water purification technologies, photocatalytic membranes, and integrated environmental treatment reactors.

G-ZnO systems demonstrate strong potential for rapid catalytic degradation under optimized irradiation conditions, especially in environments requiring fast oxidation kinetics. However, photocorrosion and structural instability remain important constraints for long-duration applications.

Cross-system comparison reveals that semiconductor optimization should be application-specific rather than universally standardized. Industrial dye remediation, pharmaceutical degradation, decentralized water purification, and hybrid photocatalytic–biological treatment systems may require different catalytic priorities.

The broader sustainability implications are substantial. Solar-driven photocatalysis may reduce dependence on chlorine-based oxidation systems, decrease chemical treatment demand, and support decentralized wastewater remediation in resource-constrained regions. Nevertheless, large-scale implementation requires addressing catalyst recovery, nanoparticle release risks, energy integration efficiency, and long-term environmental compatibility.

The findings contribute to sustainability science by demonstrating that advanced materials technologies must be evaluated through environmental systems thinking rather than isolated efficiency metrics. A highly efficient catalyst may still be environmentally problematic if synthesis pathways are energy-intensive, operational stability is poor, or nanoparticle release introduces ecological toxicity.

Theoretically, this article contributes to natural sciences scholarship by integrating semiconductor physics, environmental chemistry, nanotechnology, and sustainability analysis into a unified explanatory framework. The comparative evidence demonstrates that photocatalytic functionality emerges from interconnected physicochemical mechanisms involving electron dynamics, surface chemistry, radical generation, and environmental operating conditions.

Proposition 1: Graphene-mediated interfacial electron transfer significantly reduces electron–hole recombination and enhances photocatalytic oxidation efficiency in semiconductor nanostructures.

Graphene functions as an electron-conductive network facilitating charge separation and improving radical generation capability under irradiation conditions.

Proposition 2: Oxygen-vacancy dynamics mediate the relationship between semiconductor composition and photocatalytic stability.

Moderate oxygen-vacancy formation enhances conductivity and visible-light responsiveness, whereas excessive vacancy concentration destabilizes semiconductor structure and accelerates photocorrosion.

Proposition 3: Photocatalytic efficiency is governed by the interaction between adsorption behavior, radical generation pathways, and contaminant-specific reaction mechanisms.

Degradation outcomes depend not solely on semiconductor activity but also on pollutant accessibility and surface interaction dynamics.

Proposition 4: Sustainable environmental remediation requires balancing catalytic efficiency with physicochemical durability and environmental compatibility.

Long-term remediation success depends on operational resilience, material stability, and lifecycle sustainability rather than short-duration degradation performance alone.

These propositions integrate nanomaterials science, environmental chemistry, and sustainability-oriented engineering into a comparative framework for understanding semiconductor photocatalysis under realistic environmental conditions.

CONCLUSION

This study comparatively analyzed the photocatalytic performance of graphene-modified titanium dioxide and graphene-modified zinc oxide nanostructures for solar-driven wastewater remediation. The findings demonstrate that photocatalytic functionality is governed by interconnected physicochemical mechanisms involving charge-transfer dynamics, oxygen-vacancy behavior, surface chemistry, radical generation pathways, and nanoscale interface interactions.

The comparative evidence indicates that graphene incorporation substantially enhances photocatalytic efficiency in both TiO₂ and ZnO systems by improving electron transport, reducing recombination probability, and increasing adsorption capability. G–ZnO systems demonstrate stronger short-term degradation kinetics and rapid electron mobility, whereas G–TiO₂ systems exhibit superior long-term physicochemical stability and photocorrosion resistance.

The study contributes theoretically by integrating semiconductor physics, nanomaterials engineering, environmental chemistry, and sustainability science into a unified analytical framework explaining photocatalytic

remediation mechanisms. The findings extend existing scholarship by demonstrating that photocatalytic efficiency should not be interpreted solely through degradation percentages but through broader environmental and physicochemical performance criteria.

Empirically, the article contributes comparative interpretation of graphene-modified semiconductor systems using convergent evidence from spectroscopy analyses, degradation experiments, computational semiconductor studies, and environmental remediation literature. The findings further demonstrate that photocatalytic sustainability depends on balancing catalytic activity with structural resilience and environmental compatibility.

Technologically, the study suggests that future photocatalytic systems should prioritize nanoscale interface engineering, oxygen-vacancy optimization, and long-term operational durability. Environmentally, solar-driven photocatalysis offers substantial potential for reducing chemical treatment demand and improving wastewater remediation sustainability.

The study nevertheless contains limitations. The comparative synthesis relies on secondary experimental literature and does not include new laboratory fabrication or direct performance measurements. Future research should therefore integrate standardized comparative experiments, real wastewater matrices, pilot-scale reactor systems, and lifecycle environmental assessment to evaluate large-scale implementation feasibility.

Ultimately, this article argues that sustainable photocatalytic wastewater remediation depends not merely on semiconductor composition but on the capacity to engineer integrated nanostructured systems capable of optimizing electron transfer, physicochemical stability, radical generation, and environmental resilience simultaneously.

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