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Review Article

Recent Advancements in Zirconium Dioxide-Graphene Oxide Nanocomposites for the Photocatalytic Degradation of Phenanthrene

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs), particularly phenanthrene, pose severe environmental threats due to their toxicity, carcinogenicity, and persistent nature. Heterogeneous photocatalysis offers a sustainable pathway to mineralize such recalcitrant contaminants. Zirconium dioxide (ZrO_2) stands out as a photocatalytic medium due to its outstanding thermal stability and strong redox properties (conduction band: -1.0 eV; valence band: +4.0 eV). However, its efficiency is typically impaired by a wide bandgap and rapid recombination of electron-hole pairs. The use of cocatalysts or functional materials is effective because it enhances charge transfer, lowers recombination, and creates synergistic effects. This review is a critical analysis of how Graphene Oxide (GO) can overcome these shortcomings through the creation of ZrO_2-GO nanocomposites. The integration of GO creates a Schottky-like junction, which serves as an electron sink and, simultaneously, increases pollutants' adsorption through π-π stacking interactions with phenanthrene's aromatic rings. Contrary to the previous research, which mainly concentrated on dyes or simple inorganics, this study specifically fills the gap in knowledge on the degradation pathways, intermediate toxicity, and pathway of mineralization of complex PAHs across ZrO_2-GO-based systems. We compare recent material design approaches, such as phase engineering, green synthesis, and ternary heterojunctions, towards optimization of visible-light harvesting. Lastly, the review discusses catalyst stability under realistic wastewater conditions and the elimination of toxic products, offering a strategic roadmap for translating ZrO_2-GO photocatalysts from laboratory research to scalable environmental remediation.

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1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are amongst the environmental contaminants that pose a threat to remediation technologies because of their persistence, toxicity, and carcinogenicity (Sher et al., 2023; Montano et al., 2025). Phenanthrene, among the PAHs, is a commonly used model compound among priority pollutants because it combines three fused aromatic rings, which form an intermediate level of structural complexity and stability between low-molecular-weight bicyclic PAHs and high molecular weight, highly fused aromatic systems (Dai et al., 2025; Maddheshiya et al., 2026). Conventional methods for PAH removal, like adsorption, bioremediation, and chemical oxidation, are usually expensive, slow, or result in the formation of secondary pollutants (Omer & Moinfar, 2026; Talaie et al., 2026). As a result, heterogeneous photocatalysis has emerged as a promising alternative, where semiconductor materials are utilized to harness solar or ultraviolet radiation to mineralize organic contaminants into CO_2 and H_2O (Paiu et al., 2025).

ZrO_2 is a transition metal oxide that has gained substantial attention in this field owing to its exceptional chemical, thermal, and mechanical stability (Li et al., 2026). ZrO_2 has unique electronic properties that allow for high reduction and oxidation potential due to its naturally acidic surface properties, unlike other conventional photocatalysts, including TiO_2 and ZnO (Aziz et al., 2024). ZrO_2's distinguishing characteristics include very high reduction potential, amphoteric surface nature, and oxygen-conducting defect chemistry (Sarkar et al., 2026). ZrO_2 has a more negative conductive band minimum (CBM) (-1.0 V vs. NHE at pH 0) than anatase TiO_2 (-0.1 V), which means it is a much more capable reduction agent (Rani et al., 2022). In the meantime, the valence band maximum (VBM) is lower (around +4.0 V) than that of TiO_2 (+3.1 V), which produces much more robust thermodynamic driving force for oxidation (Li et al., 2026). ZrO_2 has acidic and basic surface sites due to its amphoteric nature (Rasal et al., 2026). Their strength is determined by the crystal phase, with the monoclinic phase of ZrO_2 as a stronger acid and base than the tetragonal phase (Butova et al., 2025). In addition, ZrO_2 tends to act as an n-type semiconductor because the oxygen vacancies could add trap levels to the bandgap (Itagaki et al., 2026).

Nevertheless, monoclinic ZrO_2 (3.2 to 5.1 eV) features an extensive bandgap, a property that confines its photoactivity to the UV light spectrum, which only harnesses a narrow solar segment penetrating Earth's surface (Meng et al., 2026). To avoid this limitation and enhance reactions between charge carriers and the supporting matrix, researchers focused on integrating GO and reduced graphene oxide (rGO) supporting matrices and electronic mediators (Chenarani & Ghaemi, 2025). Phenanthrene photodegradation is promoted through a dual-functional process through the combination of GO with ZrO_2. Firstly, the π-π interaction between aromatic rings of phenanthrene along with sp^2 clusters of GO improved pre-adsorption (Li et al., 2023). Secondly, GO acts as an electron sink by creating a Schottky-like junction at the ZrO_2-GO interfaces (Iqbal et al., 2022; Jayasinghe et al., 2022). GO also facilitates electron transfer from the ZrO_2 conduction band, thereby suppressing charge recombination and allowing the valence band (VB) to drive phenanthrene ring-opening. This synergy between ZrO_2 redox potential and GO charge transport enhances photodegradation.

In addition to the electronic benefits, the adsorption behavior of the composite is also a crucial factor for the degradation of phenanthrene. A three-ringed PAH, phenanthrene ($C_{14}H_{10}$), is a key model compound for very persistent organic contaminants. The high lipophilicity (log $K_{ow} \approx 4.46$) and extremely low aqueous solubility (≈1.29 mg/L) make it difficult to use conventional aqueous-phase photocatalysis. The hydrophobic surface affinity of the traditional metal oxide catalysts, such as TiO_2 or bare ZrO_2, typically is inadequate to effectively extract phenanthrene from the bulk solution. The ZrO_2-GO composite approach overcomes this and takes advantage of the sp^2-hybridized lattice of GO, which allows for strong π-π stacking interactions with the aromatic rings of phenanthrene, which allows pre-concentration of the pollutant at the catalytic active sites where the generation of ROS occurs (Altarawneh & Ali, 2024). Available studies indicate the strong potential of ZrO_2-GO nanocomposites, but highlight gaps and challenges that future research must fill to justify their use in phenanthrene removal. The main challenges include inadequate testing on phenanthrene, optimizing visible-light activity, and stability and mineralization in realistic matrices. The existing gap is that there is no direct evidence of ZrO_2-GO performance on phenanthrene in particular, and most ZrO_2-GO work is on dyes, inorganic pollutants, or other organics, but the vast amount of data on phenanthrene degradation research is on GO-metal composites (Chauhan et al., 2021; Mylarappa et al., 2024).

To implement ZrO_2-GO photocatalysts in real-life applications, several issues need to be solved in the process of transplanting them out of the laboratory. Band engineering, or heterojunction construction, is required to attain high visible-light absorbance with sufficient oxidative potential, as the wide bandgap of ZrO_2 hinders the use of solar energy (Huma et al., 2025). Stable ZrO_2-GO interfaces with regulated oxygen gaps and phase structure are required, as changes in these structural characteristics may cause changes in photocatalytic activity. Long-term stability and recyclability are also concerning, as photocatalysts must be resistant to fouling and photocorrosion on repeated cycles in complex wastewater conditions, rather than controlled laboratory conditions. Lastly, the pathways to full mineralization of phenanthrene and the analysis of intermediates' toxicity have not been properly investigated with the ZrO_2-GO photocatalyst, raising the question of whether the degradation process removes the hazard posed to the environment or merely transforms it into even more problematic byproducts.

This report discusses the latest trends in the area of ZrO_2-GO-based photocatalysts in the photodegradation of phenanthrene and provides an overview of the key properties, technological challenges, and innovative advancements over the past 5 to 8 years. The scope also includes the material design concepts, such as phase engineering, defect modulation, and heterojunction structure, to improve the visible light activity. It also analyzes the interfacial charge-transfer processes, adsorption-photocatalysis synthesis, and structure-activity relationships that regulate the degradation activities. The efficiency of mineralization, discovery of intermediate species, toxicity, catalyst stability, and recyclability are considered with special attention under the realistic conditions. This review aims to establish the research priorities by combining the mechanistic insights with technological challenges and suggest the way forward for future developments to make ZrO_2-GO systems applicable in practice, as the system is applied to environmental cleanup.

2. FUNDAMENTAL PROPERTIES OF ZrO_2-GO NANOCOMPOSITES

The catalytic strength of ZrO_2, great electric conductivity, and the surface area of GO are the pillars of the effectiveness of ZrO_2-GO nanocomposites. The synergy of ZrO_2-GO nanocomposites arises from complementary physical and electronic characteristics, which overcome the natural shortcoming of bare ZrO_2, such as fast charge recombination and broad bandgap (Zhao et al., 2022). GO integration increases the specific surface area, thereby creating conductive channels for transferring electrons and effective spatial charge separation (Algarni et al., 2025). Unlike the usual low surface areas (<20 m²/g) of conventional ZrO_2 nanoparticles, rGO incorporation can afford high surface areas to 120.55 m²/g or even 266.95 m²/g per unit of the final composite, facilitating pollutant adsorption by electrostatic interactions and surface sites (Kan et al., 2020). Meanwhile, the integration of GO changes the electrical characteristics of the insulating ZrO_2 by creating conductive sites with tunable conductivity ranging from 48 to 565 s/m depending on graphene loading (Kumar et al., 2025; Sadiq et al., 2026). This increase in conductivity facilitates better charge carrier kinetics, increasing the photocatalytic efficiency. Bare ZrO_2 has a large bandgap between 3.25-5.1 eV, and suffers from rapid electron recombination, but the GO component provides an electron sink, attracting the photoexcited electrons and increasing the charge carrier lifespans. This interaction can reduce the bandgap to 3.87 eV by just 4% rGO addition, and improve photodegradation. Enhanced charge separation generates more superoxide and hydroxyl radicals for pollutant degradation, with ZrO_2@MoS_2/g-C_3N_4 heterojunctions achieving degradation rates over 2.3 times higher than bare ZrO_2 (Vijayakumar et al., 2022).

Moreover, the structural and electronic properties of the photocatalysts are described. ZrO_2 exists in three distinct polymorphic forms, monoclinic (m-ZrO_2), tetragonal (t-ZrO_2), and cubic (c-ZrO_2) (Chelliah et al., 2023; Haruna et al., 2025). The monoclinic phase is the thermodynamically stable form at room temperature and atmospheric pressure, whereas the tetragonal and cubic phases require high temperatures (>1100°C) for formation. GO advances phenanthrene degradation because its aromatic lattice facilitates strong π–π stacking interaction with phenanthrene's benzene rings (El-Maaref et al., 2024). This rapid acquisition and oxidation of hydrophobic PAHs bridge the gap between simple organic models and highly complicated pollutants. Meanwhile, the ability of the system ZrO_2-GO to degrade phenanthrene has not yet been tested in direct experiments, but its efficiency on similar PAHs and aromatic dyes makes it highly likely to be effective in the case of phenanthrene. The rationale has been given for its application to phenanthrene, as it is able to produce high levels of ROS and also has the required hydrophobic adsorption sites that are not available in bare ZrO_2 (Jemai et al., 2023). ZrO_2 morphology is also vital. Photocatalytic performance of anodized ZrO_2 nanotubes strengthened at 400°C has been reported to be faster as compared to anodized ZrO_2 nanotubes that are annealed at higher temperatures because of the tetragonal and monoclinic phases and the maintenance of structural defects (Méndez-Salazar et al., 2026).

GO serves as an effective platform for the growth of inorganic nanoparticles due to its high transparency, mechanical stability, and the number of oxygen-containing functional groups, like carboxyl, hydroxyl, and epoxy groups (Chi et al., 2025). These classes enable anchoring of Zr^{4+} ions and inhibit the agglomeration of ZrO_2 nanoparticles, which is an issue that is prevalent in pure metal oxide systems (Usharani et al., 2022). Through the reduction of GO to rGO, the material transforms into a highly conductive state. In ZrO_2-rGO composites, the rGO sheets function as electron sinks, facilitating the rapid transfer of photogenerated electrons from the conduction band (CB) of ZrO_2. This process is useful in separating the electron-hole pairs and, thus, extending the charge-carrier lifetime, raising the likelihood of their involvement in the redox processes with the adsorbed phenanthrene (Wang et al., 2025). Moreover, the rGO surface is π-conjugated and can be subjected to robust π-π interactions with the aromatic rings of phenanthrene to facilitate the pre-concentration of the pollutant on the catalytically active sites (Xu et al., 2023; Zameran et al., 2025).

The main drawback of pristine ZrO_2 is its broad band gap, which prevents the effective harnessing of visible light. However, this bandgap can be strategically reduced by incorporating carbon-based materials such as GO, which introduce new electronic states within the forbidden band (Ahmed et al., 2022). As an illustration, substitutional carbon from GO can form a localized state directly above the valence band (VB), effectively narrowing the bandgap of the modified oxides down to as low as 2.9 eV. This critical modification shifts the optical absorption towards the visible region, allowing for efficient charge transfer (Matei et al., 2023). A schematic diagram is presented in Figure 1 illustrating the bandgap narrowing effect, showing the valence and conduction bands of pristine ZrO_2 versus the newly formed ZrO_2-GO nanocomposite.

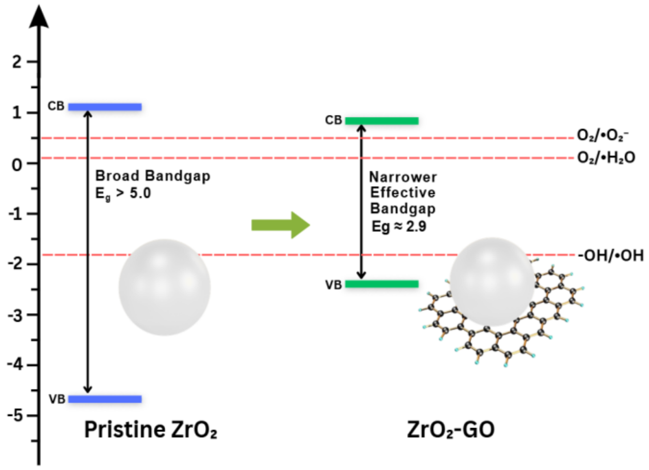

Figure 1. Schematic illustration of bandgap narrowing in the ZrO_2-GO nanocomposite compared to pristine ZrO_2.

3. PROPOSED MECHANISM OF PHENANTHRENE PHOTODEGRADATION OVER ZrO_2-GO

Photodegradation of phenanthrene on ZrO_2-GO composite occurs in a sequential process, which starts with the adsorption phase and ends with the complete mineralization phase. The phenanthrene mineralization often follows the "phthalic acid pathway" (Ma et al., 2025). The process starts with the π-π stacking of the aromatic basal plane of GO and the benzene rings of phenanthrene, followed by the reduction of the diffusion distance of reactive species to reach the pollutant and overcome the hydrophobic nature of phenanthrene (Ahmad et al., 2025). Upon irradiation, ZrO_2 absorbs photons and generates electron-hole pairs (e^-/h^+) that will recombine instantly and waste energy. As established earlier regarding charge-carrier dynamics, the electrons that are trapped on the GO surface react with the dissolved oxygen to produce $•O_2^-$, and the holes on the ZrO_2 valence band react with water or hydroxide ions to create •OH (Nguyen et al., 2020; Kotnala et al., 2026).

These ROS oxidize the adsorbed phenanthrene molecules at the 9,10-positions known as the K-region to generate 9-phenanthrenol and 9,10-phenanthrenediol as the hydroxyl product (Dai et al., 2022; Timonina et al., 2025). This first hydroxylation exposes the molecule to further oxidation to form 9,10-phenanthrenedione, which is highly reactive and easily breaks down into smaller intermediates, including 2-(2-carboxyphenyl) benzoic acid. The intermediates will be photo-oxidized to 2-formylbenzoic acid, which will be oxidized to benzene-1,2-dicarboxylic acid. The formation of 9,10-phenanthrenedione and 2-formylbenzoic acid was experimentally confirmed via GC-MS analysis in the study by Dai using potassium permanganate ($KMnO_4$) as the oxidizing chemical. The additional breakdown of larger molecules into smaller and less toxic molecules takes place as the catalytic redox reactions are continued to oxidation until the pollutant is completely mineralized into harmless CO_2 and H_2O, as shown in Figure 2. Throughout the degradation process, minimizing environmental risk because the photocatalyst aims to be promotes the total mineralization of phenanthrene into harmless end products, making this approach both potential for environmental safety relies on effective ROS production and suitable for long-term water treatment applications.

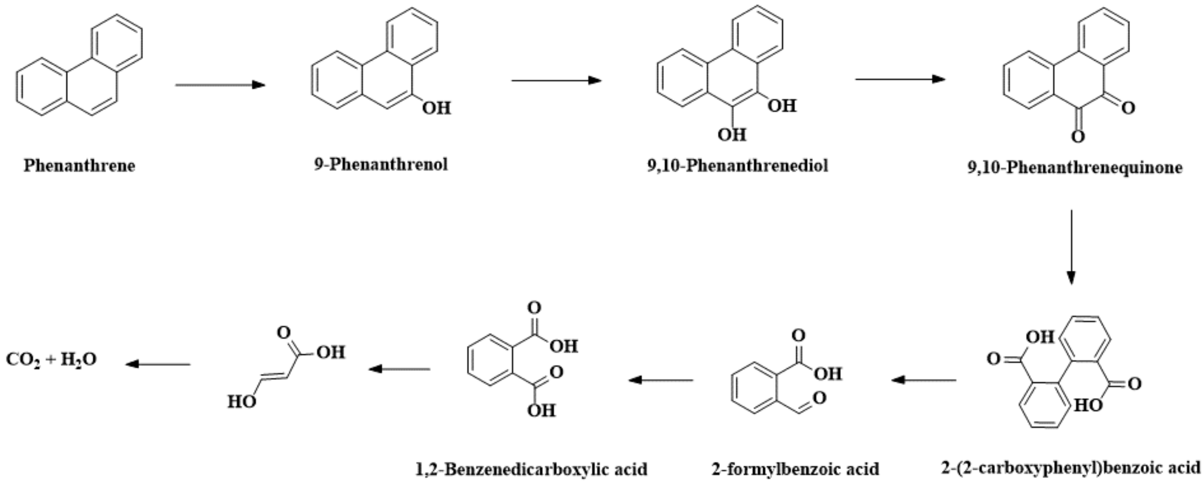

Figure 2. Mechanism proposed for the photocatalytic degradation of Phenanthrene by ZrO_2-GO nanocomposite.

Table 1. Analytical validation and ecotoxicological profile of phenanthrene degradation intermediates.

Intermediate	Analytical Detection Method	Experimental Confirmation	Toxicity Profile (Literature)	Reference
9-Phenanthrenol	GC-MS / LC-MS	Confirmed (Analogous)	High, Potential mutagenic precursor. Free (unencapsulated) 9-phenanthrenol showed a marked cytotoxicity, with its lactate dehydrogenase (LDH) release being significant at concentrations ≥ 0.25 mg/mL, in neuronal studies.	Zhang et al., (2020)
9,10-Phenanthrenedione	GC-MS	Confirmed (Direct)	High Toxicity, Induces oxidative stress (Oxy-PAH). The main constituents of particulate matter (PM), 9,10-PQ, have been associated with respiratory irritation, asthma, allergic inflammation, and lung cancer progression when inhaled.	Yang et al., (2018)
2-Formylbenzoic acid	LC-MS	Proposed by Analogy	Moderate, Intermediate metabolite. Ingestion can lead to gastrointestinal irritation, nausea, vomiting and diarrhea.	Chen et al., (2008)
Phthalic acid	HPLC / GC-MS	Confirmed (Analogous)	Low, Biodegradable end-product. Interact with androgen receptors, behaving as an androgen receptor antagonist and impacting reproductive systems, particularly male reproductive development.	Wang et al., (2022)

The thermodynamic endpoint of the pathway shown in Figure 2 is total mineralization of phenanthrene to CO_2 and H_2O, but the environmental safety of the ZrO_2-GO system in the environment is dependent upon the kinetics of the intermediate degradation steps. As indicated in Table 1, the formation of 9,10-phenanthrenedione is a short-term increase in toxicity because Oxy-PAHs may be more bioavailable and redox active than phenanthrene. Any statement of environmental 'safety' for photocatalytic remediation, then, should be backed up with coordinated monitoring of both pollutant removal and reduction of these harmful chemical side-products. At the moment, there is a great lack of knowledge: In most ZrO_2-GO studies, only high removal efficiency is reported, but there are no corresponding ecotoxicological assays (e.g., Vibrio fischeri bioluminescence tests) to prove that the remaining water is truly less dangerous. In conclusion, ZrO_2-GO composites offer a promising pathway for aromatic hydrocarbon remediation; however, their role in 'safeguarding' environmental health is strictly contingent upon achieving high mineralization rates that bypass the prolonged accumulation of toxic Oxy-PAH intermediates. Future research must shift from simple 'removal' metrics to comprehensive 'toxicity-reduction' protocols. In conclusion, ZrO_2-GO composites offer a promising pathway for aromatic hydrocarbon remediation; however, their role in 'safeguarding' environmental health is strictly contingent upon achieving high mineralization rates that bypass the prolonged accumulation of toxic Oxy-PAH intermediates. Future research must shift from simple 'removal' metrics to comprehensive 'toxicity-reduction' protocols.

The photocatalytic degradation of the ZrO_2-GO composite occurs through several coordinated steps. Upon UV irradiation, the photons excite electrons from the VB to the CB to produce electrons (e^-) and holes (h^+) as shown in Equation 1. To overcome ZrO_2's rapid recombination, GO acts as an effective electron acceptor and transfers from the ZrO_2 CB to the GO sheets, as shown in Equation 3 (Haruna et al., 2025). After this separation of charges, the remaining hole in the VB of ZrO_2 reacts with

H_2O molecules or hydroxide ions concentrated on the surface to form hydroxyl radicals •OH, as shown in Equation 2 (Iqbal et al., 2024). Simultaneously, the trapped electrons in the conductive GO surface reduce the adsorbed oxygen molecules to form the radicals of superoxide $•O_2^-$ (Binazadeh et al., 2023; Kumar et al., 2025). This is the reduction of oxygen that occurs when electrons are transferred from the conduction band of ZrO_2 to the GO surface. The direct reduction of the adsorbed oxygen on the surface sites of ZrO_2 in advance of electron transfer to the carbon matrix is shown in Equation 4. The presence of these reactive species is important in breaking down organic pollutants by attacking the surface of phenanthrene. Scavenging experiments were performed on similar ZrO_2-based composites and were used to elucidate the dominant ROS in this system. For instance, when isopropanol (as a •OH scavenger) and p-benzoquinone (as an $•O_2^-$ scavenger) were used in the studies, both hydroxyl and superoxide radicals were found to be major players in the ring-cleavage of phenanthrene. Using π-π interaction, GO concentrated phenanthrene near reactive sites, in which hydroxyl radicals assault the aromatic ring, thereby beginning the process of ring-opening and breaking down into smaller, less toxic products (Jaber et al., 2026). This heterojunction eliminates the shortcoming of pure ZrO_2 by simultaneously enhancing pollutant adsorption and generating reactive species for efficient degradation. The photocatalytic degradation process of the ZrO_2-GO composite follows through several coordinated steps, as illustrated in Figure 3.

$$\mathrm{ZrO_2} + h\nu \longrightarrow e^- + h^+ \quad (1)$$
$$\mathrm{ZrO_2}(h^+) + \mathrm{H_2O} \longrightarrow \bullet\,\mathrm{OH} + \mathrm{H^+} \quad (2)$$
$$\mathrm{GO}(e^-) + \mathrm{O_2} \longrightarrow \bullet\,\mathrm{O_2}^- \quad (3)$$
$$\mathrm{ZrO_2CB}(e^-) + \mathrm{O_2} \longrightarrow \bullet\,\mathrm{O_2}^- \quad (4)$$
$$\bullet\,\mathrm{OH} + \mathrm{Phenanthrene} \longrightarrow \mathrm{Degradation\ products} \quad (5)$$
$$\bullet\,\mathrm{OH} + \bullet\,\mathrm{O}^{2-} \longrightarrow \mathrm{H_2O_2} \quad (6)$$
$$\mathrm{H_2O_2} \longrightarrow \mathrm{H_2O} + \mathrm{O_2} \quad (7)$$
$$\bullet\,\mathrm{OH} + \mathrm{Phenanthrene} \longrightarrow \mathrm{CO_2} + \mathrm{H_2O} \quad (8)$$

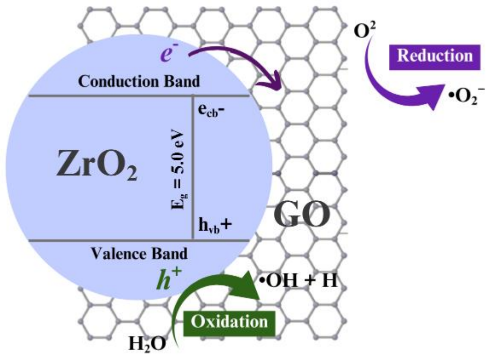

Figure 3. Charge separation in ZrO_2-GO under irradiation produces $•O_2^-$ and •OH radicals that drive photocatalytic degradation.

The characterization of the transient intermediates is achieved by prior studies and detailed analytical characterizations such as GC-MS and LC-MS, and is heavily relied upon for the purpose of validating these proposed degradation pathways. 9,10-phenanthrenedione and 1,2-benzenedicarboxylic acid are examples of products resulting from the successive ring-cleavage process, following the attack by the •OH radical. Knowing the structural breakdown is insufficient to move forward with environmental remediation, thus, the knowledge of intermediate toxicity is needed as well. The final product is complete mineralisation to CO_2 and H_2O, but intermediate products like oxygenated PAHs (oxy-PAHs) might be more acute toxic and/or mutagenic than the parent molecule phenanthrene. An urgent unmet need is to include models of toxicity testing (such as the Ecological Structure Activity Relationships (ECOSAR) program), or empirical bioassays, in future research on ZrO_2-GO systems to ensure that this sequential breakdown of the K-region in phenanthrene over time is correlated to a reduction in environmental hazard profile over time.

A critical analysis of current literature reveals that the majority of performance data for ZrO_2-GO systems reported (Table 2) comes from surrogate pollutants such as crystal violet, eosin yellow, Cr(VI). These proxies reflect key aspects of charge-carrier dynamics and bandgap narrowing but there remains the need for further direct validation for phenanthrene, a neutral, non-polar PAH. The mechanistic claim made in this study with respect to phenanthrene mineralization over ZrO_2-GO is therefore presented here in the form of a research hypothesis. Then, future research should be done on the intermediate phthalate to mineralization end products transition using GC-MS or LC-TOF-MS, specifically with ZrO_2-

GO/phenanthrene systems instead of only making inferences based on the presence of more polar dye molecules. An important point of interest in the treatment of PAHs by photocatalytic methods is the production of ‘Oxy-PAHs' like 9,10-phenanthrenedione. Analogous photocatalytic systems (such as systems based on TiO_2) have been tested under ecotoxicological conditions and show that these quinone-like intermediates may be more toxic than the parent phenanthrene molecule because of their generation of ROS in cellular compartments. In spite of that, the ZrO_2-GO system has shown potential to reduce this polluting risk since the mineralization data for the surrogate pollutants indicates a high mineralization rate, meaning that the frontier ZrO_2-GO interface is able to transform stable aromatic rings into low-toxicity dicarboxylic acids, which are more mineralizable.

4. TECHNOLOGICAL CHALLENGES IN PHENANTHRENE PHOTODEGRADATION

Despite the promising attributes of ZrO_2-GO photocatalysts, numerous challenges must be addressed to ensure practical applicability. There are problems with the inherent electronic properties, environmental factors, and recovery methods. Although GO is demonstrated to be able to overcome the intrinsic fast recombination of electron-hole pairs of bare ZrO_2 as reported in Section 2, the exact optimization of the content of GO is a crucial technological challenge (Geldasa & Dejene, 2025). An excess of GO can act as a recombination center or shadow the active catalyst surface, thereby can suppress the photocatalytic activity (Tolosana-Moranchel et al., 2019). Excessive GO exhibits strong UV-Vis absorption, creating a shielding effect that blocks incoming photons from reaching the ZrO_2 surface, which consequently reduces the generation of electron-hole pairs (Ahmad et al., 2025). High loading of the GO sheet also tends to form thick, multi-layered clusters restacked via van der Waals and π–π interactions, covering ZrO_2 active sites and hindering phenanthrene adsorption and product diffusion (Mondal et al., 2021). Meanwhile, excessive GO itself is a recombination network as this behavior is a direct consequence of the charge-carrier dynamics established in Section 2. The dense conductive pathway enables the electrons and holes to meet before reaction, subsequently resulting in a reduction of photovoltage and photocatalytic efficiency (Haruna et al., 2025).

Consequently, activity increases at optimal GO content but declines sharply at higher loading. As established in Section 2, GO has a high conductivity which is essential for electron transportation. However, at GO loads greater than the optimum, there is a 'shielding effect' and an increase in recombination centres that negate many of the benefits mentioned above. The next challenge involves addressing spectral limitations and improving solar energy harvesting in the nanocomposites. Pristine ZrO_2 is incapable of utilizing nearly 96% of the solar visible spectrum, as its absorption is restricted to the 5% UV range from the sunlight (Solomon et al., 2025). This complicates the adoption of ZrO_2-based systems in real-world situations that depend on sunlight as the primary source of energy. Although spectral response can be extended by doping and the formation of heterojunction, high efficiency in the visible and near-infrared spectrums is still a topic under research. Beyond the intrinsic chemical stability of phenanthrene, the application of suspended nanoparticles in wastewater treatment poses practical challenges in the recovery of catalyst nanoparticles after the reaction is complete.

Phenanthrene itself poses a significant problem due to its non-planar structure and is chemically stable as opposed to other PAHs like anthracene (Goettl et al., 2025). High energy is needed for the cleavage of the aromatic rings in phenanthrene, which demands the formation of high concentrations of reactive species (Brindhadevi et al., 2024). Research consistently demonstrated that phenanthrene is more resistant to degradation compared to anthracene, suggesting the half-lives in soil are between 3.51 and 9.37 hours, depending on the catalyst and radiation (Ji, 2021). Moreover, the leakage of nanoparticles into the environment can present significant harm threats to both human populations and marine life (England et al., 2024; Morshead et al., 2025). This phenomenon has resulted in the evolution of immobilized systems and magnetic photocatalysts that are capable of being easily separated magnetically (Aldeen et al., 2022).

The practical viability of ZrO_2-GO nanocomposites depends heavily on their long-term stability and recyclability. The most common indicator of stability in the studies reviewed is the percentage of degradation efficiency from reusability. High performance systems like rGO-ZrO_2 and GO/Ag_3PO_4 have been able to maintain efficiency of over 90% after 5 or more cycles. Standardization of efficiency loss is still a challenge, however, and researchers are encouraged to report not only efficiency loss but also post-reaction characterization (e.g., XRD, XPS) to help determine whether the ZrO_2-GO interface is subject to photocorrosion or surface fouling by phenanthrene intermediates during long-term operation. Despite the promising attributes of ZrO_2-GO photocatalysts, several challenges limit their practical application. As illustrated in Figure 4, these include rapid charge recombination, limited solar-light utilization, excessive GO loading, the intrinsic stability of phenanthrene, and catalyst recovery issues.

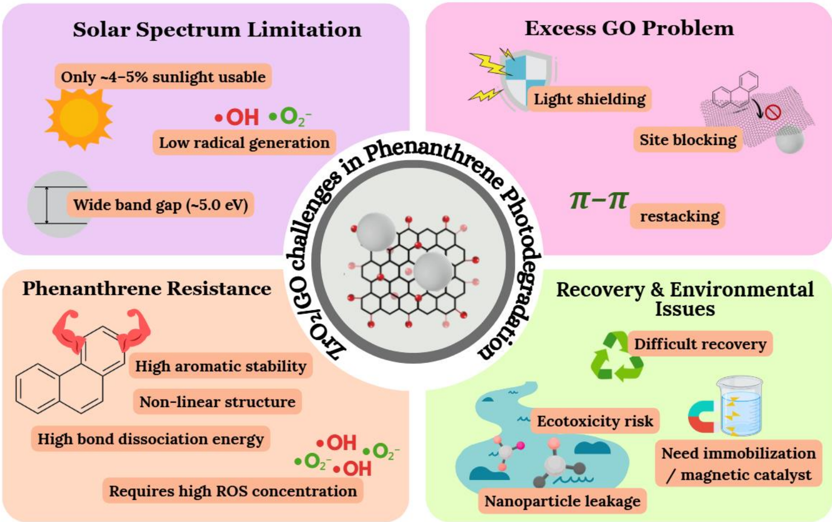

Figure 4. Schematic representation of the technological challenges limiting phenanthrene photodegradation over ZrO_2-GO photocatalysts, including rapid charge recombination, limited solar absorption due to a wide band gap, excessive GO loading effects, intrinsic phenanthrene stability, and catalyst recovery issues in aqueous systems.

5. RECENT ADVANCEMENTS IN ZRO_2-GO-BASED PHOTOCATALYSTS

Over the last 5-8 years, several new innovative methods have been created by scholars aiming to improve the activity of ZrO_2-GO photocatalysts. These are optimization of synthesis methods, development of ternary heterojunctions, and engineering of oxygen vacancies. Mechanistic improvements in ZrO_2-GO nanocomposites arise from electronic, structural, and interfacial effects that increase light harvesting, charge separation, and generation of reactive species relevant to PAH removal. GO acts as an electron acceptor/conductor, which inhibits electron-hole recombination (Prashanti & Damodharam, 2017; Majumder & Gangopadhyay, 2022). GO/rGO accepts photogenerated electrons from ZrO_2 and facilitates interfacial charge transfer, lowering recombination and increasing available oxidative holes and radical production. High specific surface area and intimate nanoparticle-sheet contact increase pollutant adsorption near reactive sites and expose hydroxyl groups that generate •OH radicals (Ali et al., 2019; Zhang et al., 2025). Studies of GO-metal PAH photocatalysts identify $•O_2^-$ and h^+ or •OH as primary oxidizing species for phenanthrene, depending on the catalyst system (Mylarappa et al., 2024).

5.1 Innovative Synthesis Methodologies

Selecting an appropriate synthesis method is essential for tailoring the properties of ZrO_2-GO composites. Certain wet-chemistry pathways are used to generate the composites, aiming at close contact of ZrO_2 and graphene derivatives, as well as at controlling ZrO_2 phase, crystallization, and porosity in order to maximize photocatalytic sites. Reported methods comparisons include hydrothermal growth, template-assisted microwave synthesis, green synthesis, co-precipitation, and others. In the case of degradation of the PAH, such as phenanthrene, a critical synthesis methodology must be selected to allow sufficient nanostructure to fit the bulky phenanthrene molecules, as well as a strong heterojunction to maintain the long-term redox reactions needed for ring-opening (Fosso-Kankeu et al., 2020).

5.1.1. Co-precipitation Method

In this technique, a precursor of zirconium (e.g., zirconyl chloride) is added to a suspension of GO, and a base (e.g., KOH) is added dropwise to keep the pH high (>10.5). The precipitate thus obtained is subjected to calcination at relatively low temperatures (e.g., 180°C) to create ZrO_2 nanoparticles attached to GO sheets (Alkhalifa et al., 2025; Das et al., 2019). Additionally, co-precipitation is frequently described as a simple, facile, and low-cost technique compared to more complex pathways (Alsubhe, 2025; Negm et al., 2025). Ensuring that ZrO_2 nanoparticles are evenly and fully densified on the GO nanosheets, forming a strong interface, the as-prepared nanocomposites have high structural stability and activity (Oppong et al., 2019; Usharani et al., 2022). This method also allows for a porous microstructure with a high number of active sites, which enhances the adsorption of pollutants (Guel et al., 2017). Conventional co-precipitation is, however, a limitation to the photodegradation of phenanthrene. While co-precipitation is simple, comparisons with other techniques, such as the hydrothermal method, are often cited for producing nanoparticles with narrower size distributions and higher crystallinity. Although traditional precipitation may have better percentage yields (e.g., 41.77% precipitation and 40.39% hydrothermal) and smaller particle sizes (13.1 nm precipitation and 17.2 nm hydrothermal), it may be affected by uncontrolled aggregation of particles (Boran & Okutan, 2023). This aggregation may hinder mesopores, such that the diffusion of large PAH molecules cannot take place to the active sites. Hence, co-precipitation is excellent for large-scale production, cost-effective, and requires treatment after synthesis for better surface accessibility for bulky pollutant degradation.

5.1.2. Hydrothermal Synthesis

The hydrothermal process is highly efficient for the simultaneous reduction of GO to rGO and ZrO_2 crystallization. This procedure typically involves heating the precursor solution in a Teflon-lined autoclave between 120°C and 180°C for several hours (Kuryliszyn-Kudelska & Dobrowolski, 2026). Hydrothermal assembly forms dense layers of ZrO_2 nanoparticles onto GO and achieves good interfacial contact and increased activity of inorganic pollutants. The hydrothermal method offers several structural and functional advantages over other synthesis pathways since it has high potential to generate well-isolated nanoparticles with a smaller size distribution than other synthesis methods, such as sol-gel or vapor phase synthesis (Sagadevan et al., 2021). Sol-gel methods permit lower temperature synthesis and exact pore size regulation, whereas the ultrasound-assisted sol-gel technique is commonly quicker, and higher purity materials are obtained as compared to standard sol-gel (Mustapha & Hjiri, 2026). It allows for the one-pot synthesis of ZrO_2 nanoparticles decorated on rGO, meaning the reduction of GO and the deposition of metal oxides occur simultaneously. Hydrothermal GO-ZrO_2 products exhibit high-quality photocatalytic activity, including a 98% removal rate (Prashanti & Damodharam, 2017). This capability is due to enhanced intensity of light absorption and decreased recombination of electron-holes, and thus, it is especially good at degrading stable aromatic rings in phenanthrene, where continual production of radicals is needed.

5.1.3. Green Synthesis

Recent trends have seen the rise of environmentally friendly synthesis routes using plant extracts, such as *Murraya koenigii* or *Prunus yedoensis*, to cap and stabilize ZrO_2 nanoparticles. These bio-compounds can promote nucleation development, charge transfer, and eliminate harmful chemical reagents (Chelliah et al., 2023). Sugarcane juice, as a non-toxic reducing agent, has been employed to generate reduced graphene oxide (rGO) in a compound (Poonpat et al., 2025). The juice contains fructose and glucose, which can reduce GO into rGO by transforming carbonyl groups into carboxylic groups throughout the hydrothermal process (Singh et al., 2018; Silva et al., 2024). More importantly, green synthesis has a direct impact on photocatalytic performances. Unlike the conventional capping agents, which must be removed, bio-organic capping agents usually introduce functional moieties onto the catalyst surface that increase the affinity of organic pollutants. The literature identifies a pronounced difference between the processes of green synthesis and conventional laboratory procedures, including hydrothermal and co-precipitation procedures, which, despite the presence of the ability to control the phase and particle sizes, usually require the introduction of synthetic bases (KOH/NaOH) or harmful reducing agents that can stabilize them. Comparable outcomes can be achieved through green synthesis using bio-compounds and renewable energy. Traditional sol-gel methods can be more complex and may result in low oxygen vacancy concentrations unless followed by high-temperature post-treatments (Benavides-Guerrero, 2025). Green synthesis is noted for being a facile, "one-pot" approach that works well at lower temperatures.

5.1.4. Microwave-assisted or Template-based Synthesis

The template-based approach frequently utilizes a triblock copolymer (like Pluronic F127) to direct the growth of metal oxide particles. In the case of ZrO_2-GO, ethanol/water is used as a solvent to dissolve the copolymer to provide a scaffold. Zirconium precursors are added to the template solution, followed by the addition of a GO suspension. The template is subsequently removed via calcination (typically between 400°C and 600°C), leaving behind a porous oxide framework anchored to the graphene sheets (Zhao et al., 2020). Microwave energy is applied to the mixture (often for as little as 3.0 minutes) to promote rapid hydrolysis, condensation, and the reduction of GO to rGO (Al-Rawashdeh et al., 2020; Benavides-Guerrero, 2025). The use of microwave irradiation facilitates stabilization of heterojunctions and oxygen vacancies, which serve as an electron trap to minimize the electron-hole recombination. Compared to the traditional paths, microwave synthesis is much faster. While a standard sol-gel aging process can take up to 8 months to achieve high defect concentrations, and hydrothermal methods require 18-24 hours, microwave-assisted reactions can be completed in minutes. Although hydrothermal synthesis produces isolation with narrow size distributions, it suffers from high production costs and long reaction times compared to the rapid microwave route (Sagadevan et al., 2021). Traditional co-precipitation is less complex and less expensive and tends to produce aggregated morphology as the particles form aggregates in the solution, but template-based synthesis provides a better dispersion of ZrO_2 on the GO nanosheets (Zhao et al., 2020).

Microwave synthesis is better in speed and porosity, whereas co-precipitation costs less; however, hydrothermal synthesis is the best method to use in phenanthrene degradation. The capability to reduce GO and crystallize ZrO_2 at the same time guarantees the greatest number of interfaces (heterojunctions), which is the key to the lowest recombination rates of electrons and holes in the course of the challenging oxidation of stable PAH rings (Chauhan et al., 2022). A hydrothermal route is slower than microwave approaches but gives the most reproducible quality of crystallites and uniform distribution to ensure high-efficiency photocatalysis. The comparative advantages and morphological differences of these synthesis routes for ZrO_2-GO/rGO photocatalysts are summarized in Table 2 and schematically illustrated in Figure 5.

Table 2. Comparative analysis of synthesis methods for ZrO_2-GO/rGO photocatalysts.

Method	Key Advantages	Limitations	Notable Performance/ Examples	References
Co-precipitation	Simple, low-cost, scalable, uniform ZrO_2 on GO, porous structure, high yield (~42%).	Aggregation blocks mesopores for bulky PAHs, less uniform sizes than hydrothermal.	Strong interfaces; good adsorption/stability for pollutants.	Usharani et al., (2022)
Hydrothermal	One-pot GO to rGO reduction + ZrO_2 crystallization, narrow size distribution, strong heterojunctions.	Time-intensive (hours); higher energy/cost.	98% PAH removal; optimal for phenanthrene ring-opening.	Iqbal et al., (2022)
Green Synthesis	Eco-friendly (plant extracts/juice); low-temp one-pot; bio-capping boosts pollutant affinity.	Variable control over phase/size; source-dependent reproducibility.	High biocompatibility; enhanced charge transfer.	Tran et al., (2022)
Microwave-assisted	Ultra-fast (minutes); high porosity/oxygen vacancies; uniform dispersion; stabilizes interfaces.	Equipment needs: potential overheating.	Rapid GO reduction; superior electron-hole separation.	Benavides-Guerrero, (2025)
Template-based	Controlled porosity/morphology (e.g., via Pluronic F127); excellent ZrO_2-GO anchoring.	Multi-step (calcination 400-600°C); template removal adds complexity.	Porous frameworks for better adsorption.	Sharma et al., (2026)
Sol-gel	Precise pore/phase control; low-temp; high purity/orientation (e.g., (100)-tetragonal ZrO_2).	Long aging (weeks-months); low defects without post-treatment; complex precursors.	Good for heterojunctions; ~85% TCH degradation.	Thakur et al., (2024)
Microwave-Hydrothermal	Combines speed (microwave) + crystallinity (hydrothermal); high dispersibility; oxygen vacancies.	Specialized equipment; precursor concentration-sensitive.	Enhanced sensing/photocatalysis; uniform nanorods	Lu et al., (2013)
Combustion/ Solution Combustion	Fast, scalable; bio-template (e.g., fruit juice) for doping (Pr-ZrO_2/rGO); high surface area.	High temps possible; byproduct management.	97% MB dye removal (96% in cycles); multifunctional	Harshitha & Suresh, (2025)

5.2. Development of Ternary and Multicomponent Heterojunctions

To further improve charge separation and visible light absorption, researchers have moved toward ternary systems that combine ZrO_2 and GO with a third component, such as a noble metal or another semiconductor.

5.2.1. Metal-Doped ZrO_2-GO

The photocatalytic activity under visible light is achievable through doping with transition metals such as Cerium (Ce) or Yttrium (Y). Indicatively, Ce-doped ZrO_2 forms empty intra-band states (Ce 4f levels) that serve as an electron bridge, enabling a "double jump" mechanism under visible light irradiation (Bortot Coelho et al., 2020). As illustrated by the degradation profiles in Figure 6A-6B ZrO_2-GO nanocomposite (0.3% Ce) achieves a degradation rate 15.98 times higher than pure ZrO_2. The rate constant (*k*) for this specific composite was calculated as 1.43×10^{-2} min^{-1} as shown in the kinetic linear fittings in Figure 6C. Photoexcited electrons trapped by the GO sheet and transferred from the ZrO_2 CB via Ce ions help hinder the electron-hole recombination rate (Haruna et al., 2025). This improved charge separation and underlying electronic behavior are further corroborated by electronic band structure calculations and partial density of states (PDOS) analyses (Figure 6D-6E).

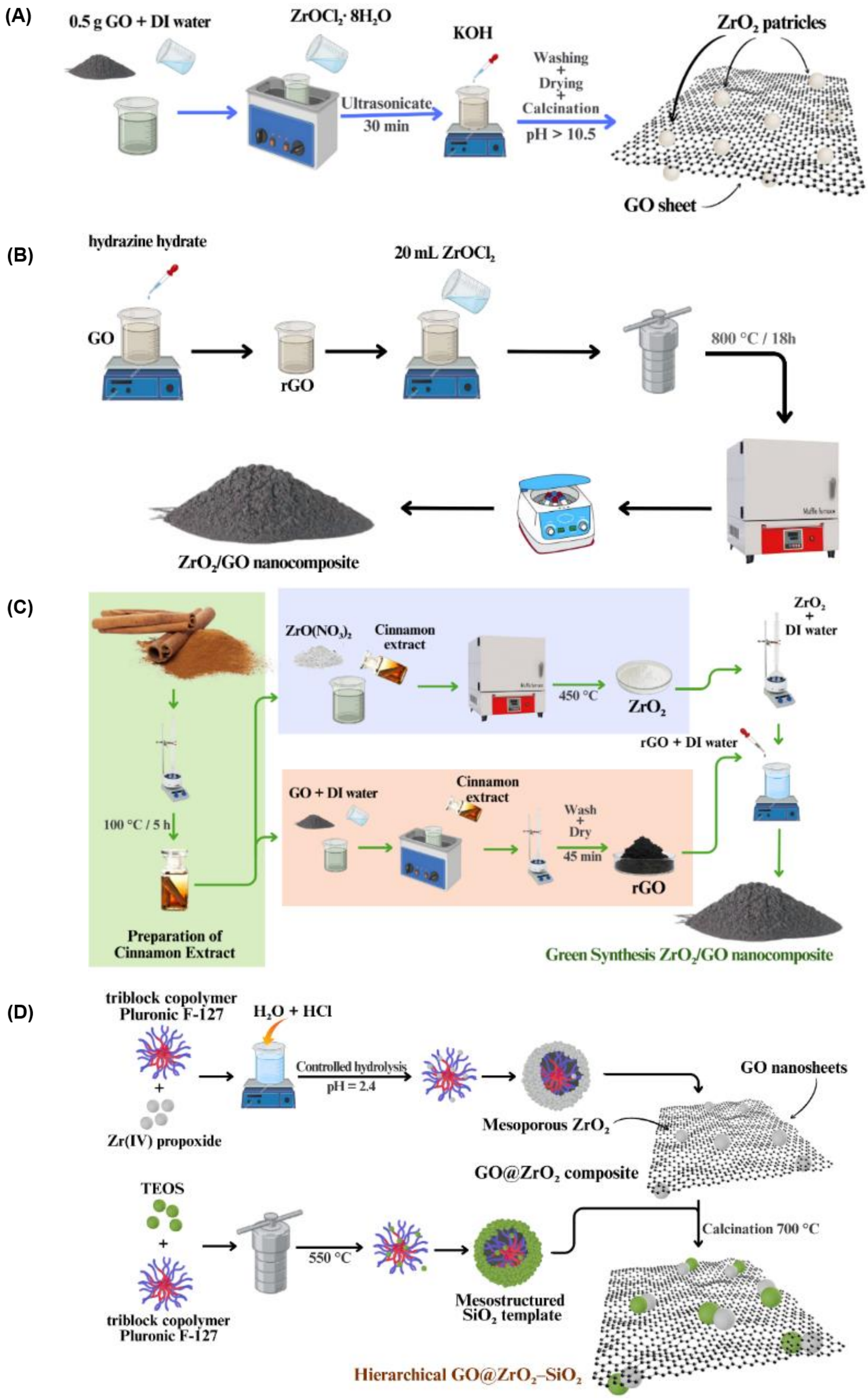

Figure 5. Schematic comparison of synthesis methodologies for ZrO_2-GO composites. (**A**) Co-precipitation results in high yields but an aggregated morphology. (**B**) Hydrothermal synthesis achieves simultaneous reduction and crystallization with uniform distribution. (**C**) Green synthesis utilizes bio-templates for eco-friendly surface modification. (**D**) Template-assisted synthesis offers rapid reaction times and high porosity, ideal for bulky pollutants.

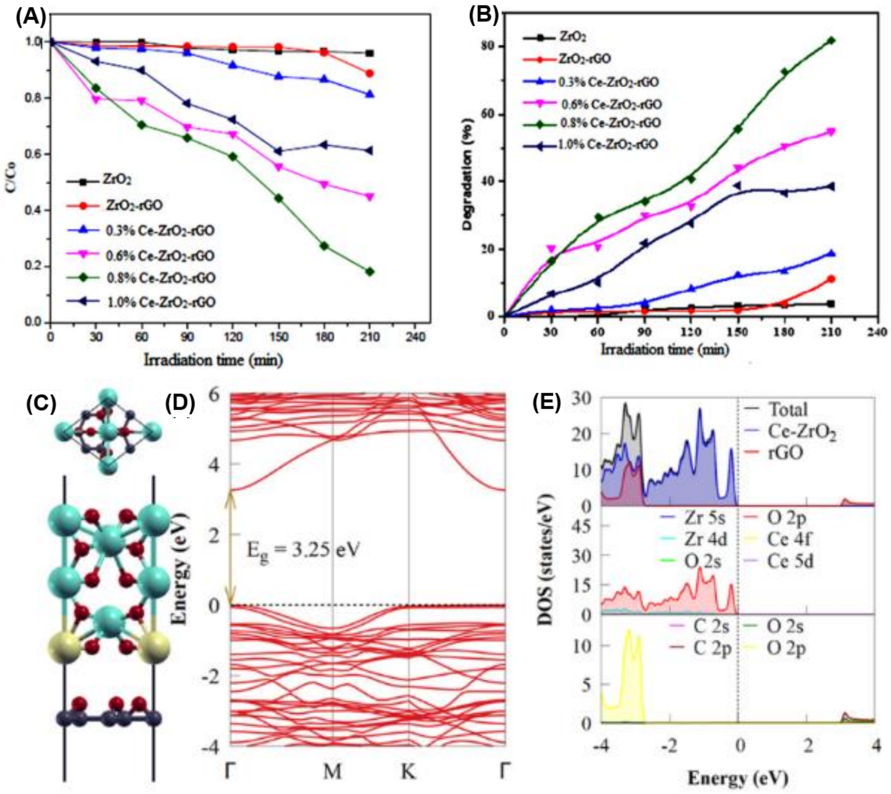

Figure 6. (**A**) C/C_0 degradation, (**B**) efficiency of photodegradation by pure ZrO_2, ZrO_2-rGO, and a series of Ce-doped ZrO_2-rGO photocatalysts. (**C**) Ce-doped ZrO_2-rGO nanocomposites. (**D-E**) Band structure calculation and PDOS of Ce-doped ZrO_2-rGO nanocomposites.

5.2.2. Semiconductor Heterojunctions

The combination of ZrO_2-GO with other semiconductors, such as TiO_2, ZnO, or WO_3, forms heterostructures that guide charge carriers in ways that minimize recombination (Dai et al., 2022). Type-I heterojunctions formed in the TiO_2/ZrO_2/rGO system enhance the efficiency of interfacial charge transfer and considerably increase the degradation efficiency for organic pollutants (De Jesús González Terán-Espinoza et al., 2025). The underlying thermodynamic pathway and charge transfer routes are schematically depicted in the proposed mechanism in Figure 7A. In a related study of a multi-component heterojunction, a ternary rGO/TiO_2ZrO_2 composite (with 20 wt% ZrO_2), demonstrated 95% of the pollutant degraded in 100 minutes. The presented rate constant was 0.0414 min^{-1}, which was much greater than the binary system because the heterojunction design enabled efficient activity when radiated by visible light (Jayasinghe et al., 2022). The intricate surface morphology and distribution features of this optimized GTZ-20 composite are illustrated via scanning electron microscopy (SEM) in Figure 7B. In another study, a $CoMoO_6/ZrO_2$/GO heterojunction synthesized via the hydrothermal method revealed mixed tetragonal ZrO_2 and monoclinic $CoMoO_6$ phases, while exhibiting the band gap of 2.29 eV, z-average of 201 ± 5 nm, and zeta potential of −36.34 ± 5 mV. At the same time, the photoactivity of $CoMoO_6/ZrO_2$/GO achieved 96 and 99.3 % degradation rate, as confirmed by FTIR, H-ESI-MS/MS, and Total Organic Carbon (TOC) analyses (Iqbal et al., 2025).

Additionally, the $Bi_8W_4O_{24}/ZrO_2$@GO nanocomposite, further enhanced by low-pressure cold plasma (LPCP) treatment, achieved a narrow band gap of 2.20 eV and a porous morphology that significantly boosted visible-light absorption. This modification led to an exceptional degradation efficiency of 98% within only 30 minutes. The synergy between the metal-oxide phases and GO, confirmed by EPR analysis, effectively generated $•O_2^-$ and •OH radicals to mineralize organic pollutants and reduce the COD of industrial wastewater by 80.41%. The $CuMoO_4$-ZrO_2/GO heterostructure, synthesized via co-precipitation with synergistic modification, tuned the crystalline structure and electronic interactions, allowing the composite to achieve a 99.5% degradation efficiency within only 30 minutes (Iqbal et al., 2026).

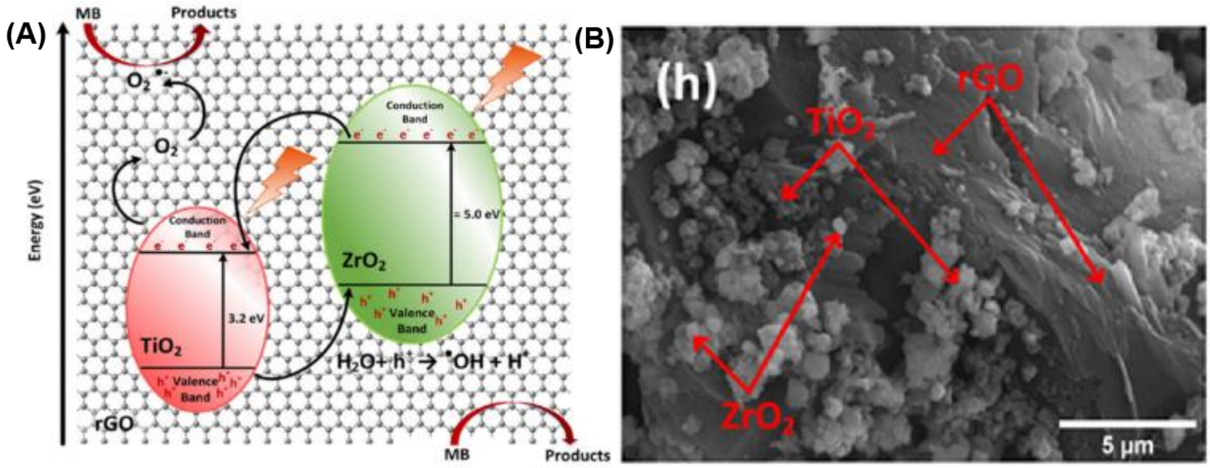

Figure 7. (**A**) Proposed mechanism of the photocatalytic for rGO/TiO_2-based ZrO_2 composites. (**B**) SEM images of GTZ-20

5.2.3. Noble Metal Loading

Coating ZrO_2 with noble metals like Platinum (Pt) or Silver (Ag) offers active sites for reduction reactions and can leverage surface plasmon resonance (SPR) to improve light harvesting (Mishra et al., 2024). This enhancement in light-trapping capabilities and the resulting narrowing of the optical bandgap (E_g) are clearly highlighted through UV-Vis diffuse reflectance spectra and corresponding Tauc plots (Figure 8E and 8F). Moreover, doping the ZrO_2 lattice with rare earth metals before compositing with GO is another strategy to narrow the bandgap. A study on 0.3% Neodymium (Nd)-doped ZrO_2-GO nanocomposites was synthesized for photodegradation, achieved 80% efficiency within 180 minutes (Mushahary et al., 2024). SEM images reveal the microstructural evolution from isolated pure ZrO_2 particles (Figure 8A) to a uniform distribution on the graphene scaffold (Figure 8B), while EDX analysis confirms the elemental composition of the nanocomposite (Figure 8C). This tailored system exhibited an accelerated pseudo-first-order rate constant of k = 4.19 min^{-1}, as derived from the kinetic linear tracking profiles (Figure 8D). The superior performance is fundamentally attributed to the introduction of sub-bandgap energy states by the Nd ions working in tandem with the high electron-transport affinity of the GO framework.

5.3. Oxygen Vacancy Engineering and Other Operational Optimization

A breakthrough in the past few years is the strategic engineering of oxygen vacancies in ZrO_2. Oxygen vacancies create in-gap energy states near the conduction band minimum, which fundamentally alter the material's energy landscape and expand its visible light absorption. The introduction of surface oxygen vacancies (OVs) into the Z-scheme $CoMoO_6$/ZrO_2/GO heterojunction via microwave cold plasma treatment significantly enhanced its fundamental photocatalytic properties (Iqbal et al., 2025). These plasma-induced OVs act as crucial electron traps and create additional conductive pathways, which effectively suppresses rapid electron-hole recombination and improves overall charge transport. Consequently, this targeted oxygen vacancy engineering optimizes the separation of photogenerated charge carriers, directly boosting the material's efficiency in degrading complex organic dyes. Through a sol-gel chelation synthesis, researchers have produced "black" or "red" zirconia with a high concentration of oxygen vacancies (up to 25.6%), allowing for room-temperature laser crystallization in ambient air. This would avoid the necessity of using high sintering temperatures (>1100°C) and would enable ZrO_2 to be used with more modern manufacturing concepts such as 3D printing (Benavides-Guerrero, 2025).

Table 3. Advancement enhancement properties of ZrO_2-GO nanocomposites.

Advancement	Description	Key Performance Indicator
Z-Scheme Heterojunction	Mimics natural photosynthesis to separate charge carriers	Enhanced stability and redox potential
S-Scheme Transfer	Optimized charge transport using internal electric fields	Improved electron extraction and transport
Oxygen Vacancies	Creation of mid-gap states near the CB	Visible light absorption up to 405 - 532 nm
LPCP Treatment	Low-pressure cold plasma for surface modification	5-6% increase in degradation efficiency

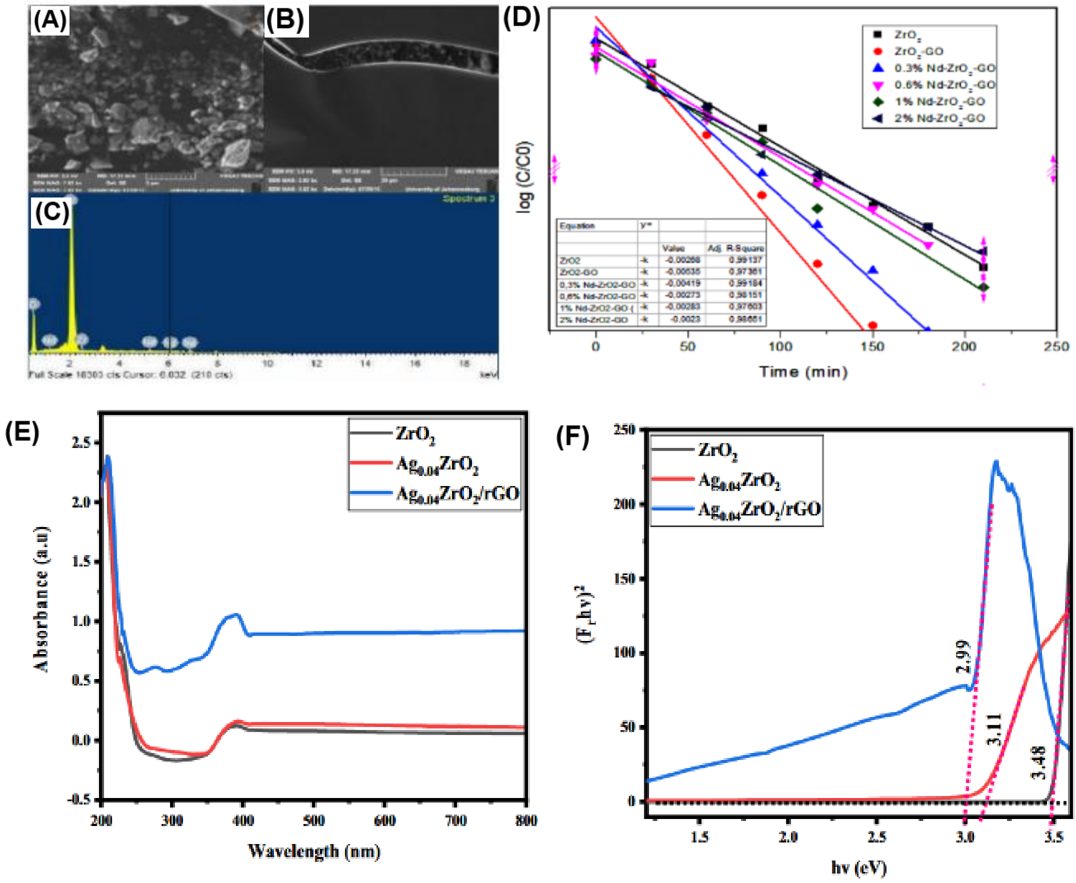

Figure 8. SEM image of (**A**) ZrO_2, (**B**) Nd doped ZrO_2-GO, and (**C**) EDX spectrum of Nd doped ZrO_2-GO. (**D**) Kinetics studies of Nd doped ZrO_2-GO catalysts. (**E**) UV–Vis and (**F**) Eg of ZrO_2, Ag0.04ZrO_2, and Ag0.04ZrO_2/rGO photocatalysts.

6. PERFORMANCE METRICS AND OPERATIONAL OPTIMIZATION

The performance of ZrO_2-GO photocatalysts is highly dependent on operational parameters, so optimization is required for the best result. The pH has a significant effect on the performance of the nanocomposites. The breakdown of phenanthrene is also very sensitive to the pH of the medium. In most ZrO_2-GO systems, a neutral pH (approximately 7) proves to be the best pH to facilitate the removal of PAHs since it balances the surface charge of the catalyst and formation of radical species (Ji, 2021; Haruna et al., 2025). Nevertheless, for certain pollutants such as picric acid, acidic conditions (pH 3) have shown 100% degradation within 15 to 30 minutes, likely due to variations in the adsorption of negatively charged moieties. Regarding catalyst dosage, the research suggests that an optimal loading (0.5 g/L or 20 mg per 100 mL) offers sufficient active sites without causing excessive light scattering. In addition to this concentration, the turbidity of the solution may reduce the penetration of light and, hence, decrease the degradation rate (Jaber et al., 2026). The completeness of mineralisation is best indicated by the percentage of TOC removed. There are a few studies on the degradation of Eosin Yellow, MB or other similar proxy pollutants over ZrO_2-GO to report TOC removal efficiencies well above 80%. Some studies of the degradation of Eosin Yellow, MB or other similar proxy pollutants over ZrO_2-GO have reported the TOC removal efficiency over 80%. This indicates that the ZrO_2-GO composite is not only capable of changing the molecular structure (decolorization/partial oxidation) but is also able to provide the deep oxidation necessary to convert complex aromatic structures to inorganic CO_2. This high mineralization potential is very beneficial compared to bare metal oxides, which may have incomplete degradation and secondary metabolites that may be toxic. The quantitative benchmarking (quantum efficiency, TOC removal) for phenanthrene is however under-reported in literature than for organic dyes, and needs to be determined in future by standardizing the approach.

Also, the selection of the light source influences the kinetics of the degradation greatly. Although UV irradiation is very efficient with wide-bandgap ZrO_2, the recent developments have managed to apply the nanocomposites to organic pollutants (100% degradation) under the sun and under visible light (Usharani et al., 2022). rGO-ZrO_2 nanocomposites have achieved 100% degradation of organic pollutants under visible and sunlight conditions, proving their potential for sustainable environmental remediation. While many studies utilize the apparent first-order rate constant (k_{app}) to describe phenanthrene degradation kinetics, relying solely on this parameter for inter-study comparison has significant limitations. Under the Langmuir–Hinshelwood model, k_{app} is dependent on both the initial pollutant concentration C_0 and the adsorption equilibrium constant (K). Therefore, a higher k_{app} obtained at lower C_0 does not necessarily indicate superior photocatalytic performance compared to a lower value measured at higher concentrations. Where applicable a normalized parameter, the specific degradation rate, has been included in Table 2 for more meaningful benchmarking. Concentration independent metrics like quantum efficiency (Φ), quantum yield and total organic carbon (TOC) removal should also be further stressed for future studies to evaluate the photocatalytic efficiency and phenanthrene mineralization. A comprehensive schematic map integrating these operational parameters, interfacial charge separation dynamics, radical generation pathways, and material optimization strategies is presented in Figure 9.

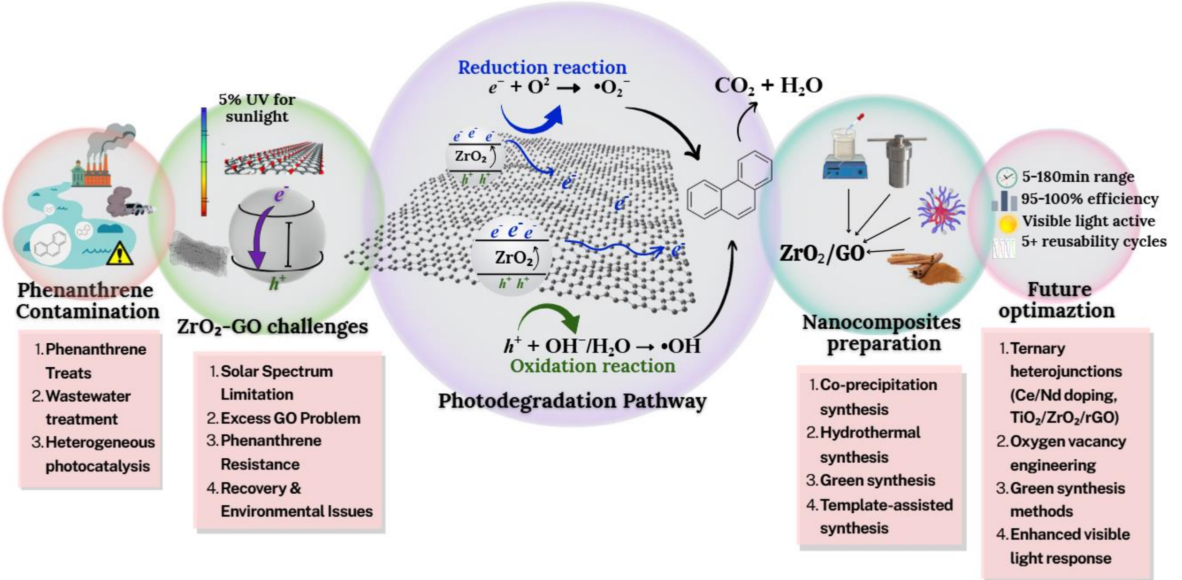

Figure 9. Schematic illustration of the enhanced photocatalytic performance of ZrO_2-GO nanocomposites for phenanthrene degradation, highlighting interfacial charge separation, reactive oxygen species ($\bullet O_2^-$ and •OH) generation, photodegradation pathways toward CO_2 and H_2O mineralization, key material challenges, synthesis strategies, and future optimization approaches.

7. INSIGHTS INTO FUTURE TRENDS

The future of this area is sustainable synthesis, multi-functional applications and defect engineering. Plant extracts and natural reducing agents have received a new focus. Plant extracts such as *Murraya koenigii* and sugar cane juice can be used as reducing and capping agents (Khorsand Zak et al., 2026). This approach avoids toxic chemicals like hydrazine while altering the shape of the nanoparticles and tuning the size for better performance. Aside from environmental remediation, multifunctional applications are trending, as these photocatalysts are being explored for solar fuel generation, such as H_2 evolution and CO_2 reduction, radiation shielding, and biosensing (Mondal et al., 2021; Hassan et al., 2025). For instance, Co-doped ZrO_2 nanoparticles are under development to serve both in photocatalytic processes and in attenuating gamma radiations (Shahbaz et al., 2026). Additionally, phase control and defect engineering are becoming viable directions for the further enhancement of photocatalysts.

The next direction in research is the oxygen vacancy engineering and the ability to control the polymorphic transition of the monoclinic to tetragonal phase. The transformation of the crystalline phase by annealing at 400°C is not only useful because it helps restructure the substance and increase the number of active sites, but also enhances the efficiency of hydroxyl radical generation during the catalytic reaction. Moreover, on fully understanding the semiconductor characteristics of GO, researchers are targeting an in-situ characterization method that can sense atomic changes at the atomic level throughout the photocatalytic process (Lu et al., 2021). The main challenge is to improve rGO conductivity, and the π-conjugation structure is necessary for high electron mobility. This can be enhanced by higher reduction processes or by doping the GO structure with heteroatoms like nitrogen or phosphorus that can be used to recover the electronic conductivity (Ahmad et al., 2025). An integrated architectural roadmap outlining these future strategic frontiers and material enhancement pathways is conceptually illustrated in Figure 10.

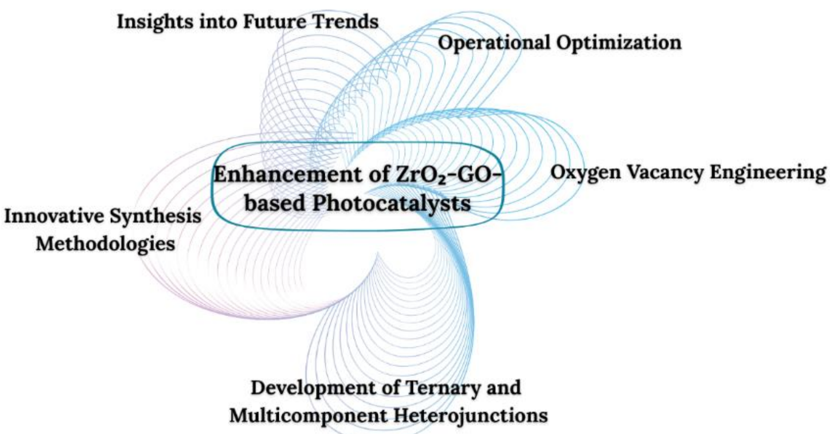

Figure 10. Demonstrates various strategies for ZrO_2-GO photocatalytic activity enhancement.

To contextualize the photocatalytic potential of ZrO_2-GO for phenanthrene degradation, the performances of GO-metal photocatalysts are reported (Farghly et al., 2025). While the literature lacks direct evidence of ZrO_2-GO degrading phenanthrene specifically, performance data from GO-metal photocatalysts and ZrO_2-GO tests on other organics can serve as indispensable benchmarks. The ROS behaviour shown by ZrO_2-GO for other pollutants can be inferred that a similar radical pathway is responsible for the degradation of phenanthrene, but with different adsorption behaviours on the surface due to the non-polar nature of phenanthrene. A brief comparison of the reported performances of photocatalysts on phenanthrene (when using GO-metal systems) and the typical performance of ZrO_2-GO on other substrates is as follows. As shown in Table 4, the ZrO_2-GO system has demonstrated exceptional degradation rates for various organic pollutants. Although direct studies focusing on phenanthrene are notably sparse in this table, the high performance observed for other aromatic and recalcitrant compounds (e.g., phenanthrene, picric acid, crystal violet dye, congo red) underscores the potential of ZrO_2 heterojunctions in treating complex wastewater matrices containing PAHs.

Table 4. Summary of photocatalytic performance, experimental conditions, and degradation performances of various ZrO_2-GO-based nanocomposites for the removal of Phenanthrene and other environmental pollutants.

Catalyst	Target and conditions	Reported degradation efficiency	Rate or note	Normalized Performance Indicators (Specific Degradation Rate: $mg{\cdot}L^{-1}{\cdot}g^{-1}{\cdot}min^{-1}$) Specific Rate: $\frac{C_0 - C_t \times Volume}{Catalyst\ mass \times Time}$	TOC Removal (%) / Stability (Cycles)	References
rGO/ZrO_2	Rose Bengal (RB) dye,20 ppm, 180 mi UV	76% degradation	Follows Pseudo-first-order kinetics. Apparent k = 0.0375 min^{-1}	0.084	91.56%, 5 Cycles, 97% (DPPH)	Mylarappa et al., (2024)
GO/Ag_3PO_4 (3 wt% GO)	Phenanthrene, visible light, 5 min, Catalyst dosage: 1 g/L; Pollutant concentration: 1 mg/L	100% degradation	Apparent k = 1.21 min^{-1}; high recyclability	0.143	N.A. Good activity retained after 6 cycles	Yang et al., (2018)
GO-Bi_2MoO_6	Phenanthrene, pH 9, 125 min	53% degraded in 125 min	Optimal conditions; high GO surface deposition (47.16% carbon).	3.533	N.A.	Fosso-Kankeu et al., (2020)
$Gd_2O_2CO_3$•ZnO•CuO	Phenanthrene, 0.4 gL^{-1}	99.6% degraded in 180 min	Optimum dosage 0.4 g/L for composite. Higher removal vs single oxides; L-H pseudo first-order kinetics, k_{app} 0.06 min^{-1}	0.277	100% removal in 120 min under optimal conditions.	Mukwevho et al., (2019)

rGO-ZrO_2	Picric acid, (200 mg/L), pH 3, UV (254 nm)	100% in 30 min	High activity attributed to oxygen-deficient phases and OH groups	0.333	90% after 5 cycles	Usharani et al., (2022)
GO-ZrO_2	Cr(VI), Sunlight, 70 min	98% removal	Dense ZrO_2 coating on GO sheets	6.53	>95% after 3 Cycles	Prashanti & Damodharam, (2017)
ZrO_2/ Fe_2O_3/ rGO	Methylene Blue (MB), 10 mg/L, visible light, 10 mg catalyst dosages	99 % in 80 min	0.1085 min^{-1} rate, rGO increasing specific surface area and high electron mobility	24.75	95% after 5 cycles	Anjaneyulu et al., (2019)
Ce-ZrO_2rGO	Eosin Yellow, 20 mg/L, visible light, 100mg catalyst dosages	83% in 210 min	Narrows bandgap of ZrO_2 and creates an internal electric field, 0.8% Ce-ZrO_2-rGO with 8.11×10^{-3} min^{-1} rate (pseudo-first-order kinetics)	0.079	High Stability (Confirmed via AIMD simulations and thermal analysis)	Haruna et al., (2025)

The high repeat rate of phenanthrene, for example, GO/Ag_3PO_4 in 5 min, was used under visible light, and the reaction observed pseudo-first-order kinetics (Yang et al., 2017; Chauhan et al., 2021). ZrO_2-GO composites exhibit extremely high degradation of other organics (up to 100% in certain cases), and so can be useful in PAH degradation when direct tests are not done (Ali et al., 2019). The first and important step is adsorption because of the hydrophobicity of phenanthrene and the large specific surface area of rGO. The molecules of phenanthrene are concentrated on the catalytic surface by π-π and hydrogen bonds beforehand (Lian et al., 2021; Xu et al., 2023; Gao et al., 2026). There are also transfers to ZrO_2 systems where the pre-concentration occurs with porous supports of TiO_2 on silica aerogel (Oppong et al., 2019; Tiryaki et al., 2023).

8. SUMMARY AND OVERVIEW

Recent progress in the photocatalysts based on ZrO_2-GO has offered a wide range of tools with which to degrade recalcitrant PAHs such as phenanthrene. Through the unprecedented chemical stability and redox potential of zirconium oxide coupled with the high surface area and conductivity of graphene oxide, there has been the development of materials that are not only effective in the visible light but also long-term mechanically and thermally stable. The creation of ternary heterojunctions and the optimization of oxygen vacancies are encouraging measures to curb recombination and spectral limitations of charge carriers, but optimization of the systems in different environments is still a challenge. Although there are still scaling issues when it comes to large-scale applications and the collection of catalysts, the transition to magnetic-based systems and immobilized membranes presents a successful direction. A combination of experimental data and theoretical modelling is still offering sensitive information on the degradation pathways of phenanthrene and gives insights into degradation pathways, which can be used to inform rational catalyst design. Nevertheless, more work is required to bridge the gap between theoretical predictions and experimental realities. Further studies are required to develop next-generation photocatalysts that are more efficient, sustainable, and environmentally friendly. In general, ZrO_2-GO composites showcase a bright future for the current endeavor to safeguard the health and environment of people against the dangerous impact of PAHs.

Several avenues for future work stand out. The photocatalytic performance of ZrO_2-GO against phenanthrene should be tested systematically under UV, visible, and simulated solar irradiation, with close attention paid to degradation kinetics and the degree of mineralization achieved in each case, while varying the rGO loading ratio, the crystalline phase of ZrO_2, and the density of oxygen vacancies to link structural characteristics to the type and yield of reactive oxygen species produced, as probed through scavenger trapping experiments. Since many ZrO_2-based systems remain largely UV-active, introducing visible-light sensitizers or coupling ZrO_2-GO with narrow-bandgap semiconductors to form heterojunctions could broaden their usability under natural sunlight, and any such modification should be assessed alongside long-term mechanical stability and recyclability, as a catalyst's real-world value depends as much on durability and reusability as on photocatalytic efficiency. Finally, defining optimal operating windows as including solution pH, catalyst dosage, and light intensity, across both simulated and real industrial wastewater will be key to moving this technology from the lab to practical application, paired with efforts to identify transient degradation intermediates and evaluate their toxicity, since incomplete mineralization can sometimes generate byproducts more harmful than phenanthrene itself taken together, these efforts would help the field converge on standardized, comparable testing protocols for graphene-based phenanthrene photocatalysis, something that is currently lacking.

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CONFLICT OF INTEREST
The authors declare no conflicts of interest.

AUTHOR CONTRIBUTION
Aishaljit Singh: Conceptualization, Methodology, Data collection, Data analysis, and Writing original draft. Suriani Abu Bakar: Conceptualization, Supervision, Review, Editing, and Correspondence author responsibility. Ghani Ur Rehman: Visualization, Conceptualization, Supervision, Manuscript review, Writing, Reviewing and Editing. Azmi Mohamed: Supervision, Review and Editing. Zeeshan Khan: Data validation. Ratno Nuryadi: Conceptualization, research design consultation. Hotaf Hassan Makki: Review and Editing. Muqoyyanah: Software, Validation.

DATA AVAILABILITY
Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

DECLARATION OF GENERATIVE AI
Not applicable.

ETHICS
Not applicable.

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