A Comprehensive Review of ZrO_2-Based Nanomaterials for Photocatalytic Dye Degradation

Lokesh Mudarapu[a], K. Hema Latha[b], Dr. Korupolu Nagu[c], Sandhya Rani Nayak[a], Ambika Mancha[a], B.B.V Sailaja[a*]

[a] Department of Chemistry, Andhra University, Visakhapatnam, Andhra Pradesh, 530003

[b] Dadi institute of Engineering and Technology, BS&H department, Anakapalle, 531002

[c] Department of Chemistry, Aditya degree and Pg college (A), Kakinada, 533003

Abstract

The discharge of dye-polluted effluents from textile and related industries poses a serious environmental threat due to their toxic and non-biodegradable nature. Photocatalysis based on semiconductor nanomaterials has emerged as an effective and environmentally sustainable approach for the removal of organic dyes from wastewater. Zirconium dioxide (ZrO_2) has recently attracted increasing attention as a photocatalyst because of its excellent chemical stability, non-toxicity, and strong resistance to photo corrosion. This review provides a comprehensive overview of recent advances in ZrO_2-based nanomaterials for photocatalytic dye degradation. The crystal structure, physicochemical properties, and synthesis strategies of ZrO_2 nanomaterials are systematically summarized, followed by a detailed discussion of the photocatalytic degradation mechanisms. The photocatalytic performances of pristine, doped, and composite ZrO_2-based systems are critically compared, highlighting the importance of elemental doping and heterojunction engineering in enhancing visible-light activity and suppressing electron-hole recombination. Key challenges, including limited solar light utilization, catalyst recyclability, and large-scale applicability, are also discussed. Finally, future perspectives are outlined to guide the rational design of efficient ZrO_2-based photocatalysts for sustainable wastewater remediation

Keywords: Zirconium dioxide (ZrO_2) nanomaterials; Semiconductor photocatalysis; Organic dye degradation; Wastewater remediation; Visible-light-driven photocatalysts.

Introduction

Rapid industrial growth and urban expansion have significantly contributed to the deterioration of water resources, mainly through the discharge of untreated or partially treated industrial effluents. Synthetic organic dyes released from textile, leather, paper, plastic, and pharmaceutical industries are among the most problematic water pollutants due to their high visibility, chemical stability, and resistance to natural degradation (Figure 1). Even at low concentrations, these dyes can obstruct light penetration in water bodies, disturb aquatic ecosystems, and pose serious risks to human health because of their toxic, mutagenic, and carcinogenic properties [1].

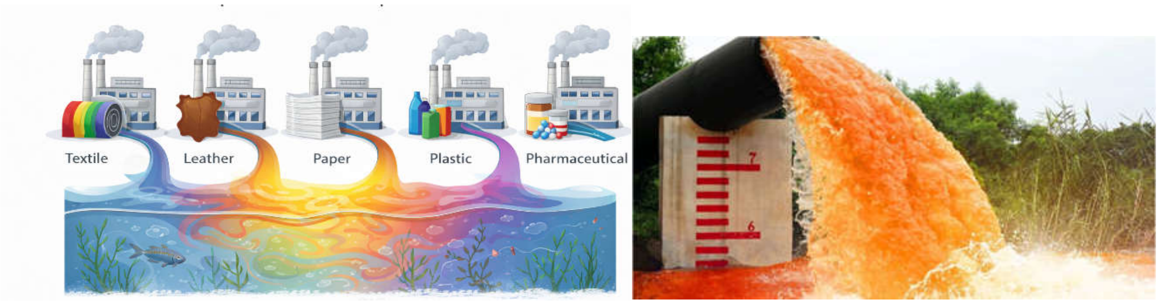


Figure 1. Major industrial contributors to synthetic organic dye pollution in water bodies

Conventional dye removal techniques such as adsorption, coagulation–flocculation, biological treatment, and chemical oxidation have been extensively employed in wastewater treatment. However, these approaches often suffer from inherent limitations, including incomplete mineralisation, high operating costs, secondary pollution, and sludge generation. Consequently, there is a pressing need for sustainable and environmentally benign technologies capable of completely degrading dye pollutants into non-toxic end products such as CO_2 and H_2O [2,3].

Semiconductor-based photocatalysis has emerged as a promising advanced oxidation process for wastewater remediation. This technique utilizes light energy to activate photocatalysts, generating electron–hole pairs that produce highly reactive oxygen species, including hydroxyl ($\bullet OH$) and superoxide ($\bullet O_2^-$) radicals. These reactive species effectively oxidize and decompose complex dye molecules, offering high degradation efficiency and catalyst reusability [4-7].

Among various semiconductor materials, zirconium dioxide (ZrO_2) has attracted growing interest due to its excellent chemical and thermal stability, non-toxic nature, and resistance to photo corrosion. ZrO_2 exists in monoclinic, tetragonal, and cubic phases, each exhibiting distinct physicochemical properties that influence photocatalytic behaviour. Despite these advantages, the wide band gap of ZrO_2 restricts its photoactivity mainly to the ultraviolet region, limiting its efficiency under solar or visible-light irradiation [8].

To overcome this drawback, several modification strategies such as metal and non-metal doping, heterojunction construction, and composite formation have been developed to enhance visible-light absorption and suppress charge carrier recombination. Recent studies have demonstrated that both pristine and modified ZrO_2 nanomaterials show promising performance in degrading various organic dyes, including methylene blue, methyl orange, rhodamine B, and Congo red [9-11].

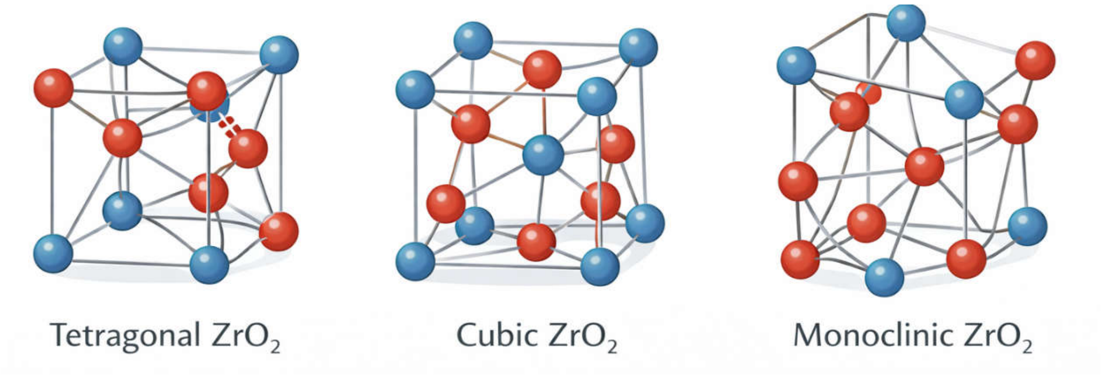
This review critically summarizes recent advances in ZrO_2-based nanomaterials for photocatalytic dye degradation, focusing on synthesis methods, structural and optical properties, degradation mechanisms, and performance enhancement strategies, while highlighting current challenges and future research directions.

2. Properties of ZrO_2 Nanomaterials

Zirconium dioxide (ZrO_2) is a wide band gap semiconductor that exhibits a combination of outstanding physicochemical properties, making it a promising material for environmental remediation and photocatalytic applications. ZrO_2 is well known for its excellent chemical inertness, high melting point (≈ 2700 °C), superior mechanical strength, and remarkable resistance to corrosion [8]. These characteristics enable ZrO_2 nanomaterials to retain their structural and functional stability even under harsh reaction conditions, which is essential for long-term photocatalytic performance.

2.1 Crystal Structure and Phases

ZrO_2 exists in three primary crystalline phases depending on temperature and particle size: monoclinic, tetragonal, and cubic. The monoclinic phase is thermodynamically stable at room temperature, while the tetragonal and cubic phases are typically stable at elevated temperatures. However, when ZrO_2 is synthesized at the nanoscale, the tetragonal and cubic phases can be stabilized at ambient conditions due to size-induced surface energy effects. The stabilization of these high-symmetry phases is particularly beneficial for photocatalytic applications, as they generally exhibit enhanced surface reactivity, improved charge carrier mobility, and better structural uniformity compared to the monoclinic phase [8,12].



2.2 Optical Properties

ZrO_2 possesses a wide band gap in the range of approximately 5.0-5.5 eV, which restricts its intrinsic light absorption primarily to the ultraviolet region. This wide band gap is a major limitation for solar-driven or visible-light photocatalytic applications. To address this challenge, various strategies such as defect engineering, metal and non-metal doping, and the formation of heterostructures or composites have been employed. These modifications introduce localized energy states within the band structure, effectively narrowing the band gap and extending light absorption into the visible region, thereby improving photocatalytic efficiency under broader irradiation conditions [9-11].

2.3 Surface Properties

The surface characteristics of ZrO_2 nanomaterials strongly influences their photocatalytic activity. Nanoscale ZrO_2 typically exhibits a high specific surface area, strong surface acidity, and a significant concentration of oxygen vacancies. These surface features enhance the adsorption of dye molecules and facilitate interfacial charge transfer processes. In particular, oxygen vacancies act as active sites for molecular oxygen adsorption and activation, promoting the formation of reactive oxygen species such as hydroxyl and superoxide radicals, which play a critical role in dye degradation [5-11].

2.4 Chemical and Thermal Stability

One of the key advantages of ZrO_2 as a photocatalyst is its exceptional chemical and thermal stability. ZrO_2 demonstrates strong resistance to photo corrosion, chemical attack, and thermal degradation, even after prolonged irradiation and repeated reaction cycles. This high stability enables the reuse of ZrO_2-based photocatalysts without significant loss of activity, making them highly attractive for practical and sustainable wastewater treatment applications [1-12].

3. Characterization of ZrO_2 Nanomaterials

Comprehensive characterization of ZrO_2-based nanomaterials is essential for understanding the relationship between structural features, physicochemical properties, and photocatalytic dye degradation performance. In review articles, characterization results reported in the literature are critically discussed to explain variations in photocatalytic efficiency.

3.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is widely used to determine the crystal structure and phase composition of ZrO_2 nanomaterials, including monoclinic, tetragonal, and cubic phases. Classical studies established the phase transformation behaviour of zirconia and its dependence on particle size and dopant incorporation [8]. Recent investigations further demonstrate that stabilization of the tetragonal phase at the nanoscale, particularly in doped and composite ZrO_2 systems, enhances photocatalytic activity by improving surface energy and charge transport properties [13].

3.2 Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

SEM and TEM analyses provide valuable insights into surface morphology, particle size distribution, and agglomeration behaviour. Early studies correlated nanoscale particle morphology with enhanced surface area and catalytic performance [12]. More recent reports reveal that well-defined nanostructures and clear heterojunction interfaces observed by TEM play a crucial role in facilitating efficient charge separation and improved dye degradation efficiency [14].

3.3 Energy-Dispersive X-ray Spectroscopy (EDX) and X-ray Photoelectron Spectroscopy (XPS)

EDX and XPS are commonly employed to confirm elemental composition and surface chemical states of ZrO_2 nanomaterials. Foundational studies demonstrated the role of dopant incorporation and surface chemistry in modifying photocatalytic behaviour [9]. Recent XPS-based studies highlight the importance of oxygen vacancies and surface defect states in enhancing visible-light absorption and reactive oxygen species generation [15].

3.4 UV–Visible Diffuse Reflectance Spectroscopy (UV–DRS)

UV–DRS is used to evaluate the optical properties and band gap energy of ZrO_2 nanomaterials. Early band structure studies established the wide band gap nature of ZrO_2 and its limitation to

UV-light activity [10]. Recent research shows that doped and composite ZrO_2 systems exhibit a red shift in the absorption edge, indicating improved visible-light utilization and enhanced photocatalytic dye degradation performance [16].

3.5 Photoluminescence (PL) Spectroscopy

PL spectroscopy provides information on the recombination behaviour of photogenerated charge carriers. Classical photocatalysis studies correlated PL emission intensity with electron–hole recombination rates [1]. Recent reports on modified ZrO_2 photocatalysts demonstrate that reduced PL intensity is associated with effective charge separation induced by dopants and heterojunction formation, leading to superior photocatalytic activity [17].

3.6 Brunauer–Emmett–Teller (BET) Surface Area Analysis

BET analysis is used to determine the specific surface area and porosity of ZrO_2 nanomaterials. Earlier studies established that higher surface area enhances adsorption capacity and photocatalytic efficiency [11]. Recent investigations confirm that mesoporous ZrO_2-based nanostructures with increased surface area provide more active sites and significantly improve dye degradation kinetics [18].

4. Synthesis Methods of ZrO_2 Nanomaterials

The physicochemical properties of ZrO_2 nanomaterials, including particle size, morphology, crystal phase, and surface area, are strongly influenced by the synthesis route employed. Selecting an appropriate preparation method is therefore crucial for tailoring ZrO_2 nanomaterials for photocatalytic dye degradation applications. Several synthesis techniques have been widely reported, each offering distinct advantages and limitations [19–21].

4.1 Sol–Gel Method

The sol–gel method is one of the most commonly employed techniques for the synthesis of ZrO_2 nanomaterials due to its versatility and excellent control over material properties. In this process, zirconium precursors such as zirconium alkoxides or zirconium salts undergo hydrolysis followed by condensation reactions to form a homogeneous sol, which gradually transforms into a gel. Subsequent drying and calcination of the gel result in the formation of ZrO_2 nanoparticles [22,23].

This method offers precise control over particle size, composition, and homogeneity, often yielding high-purity nanomaterials at relatively low processing temperatures (Figure 2).

However, the sol–gel route typically requires longer processing times and the use of organic solvents, which may increase cost and environmental concerns [21].

Figure 2. Schematic illustration of the sol–gel synthesis route for ZrO_2 nanomaterials.

4.2 Hydrothermal Method

The hydrothermal method involves the crystallization of ZrO_2 precursors in a sealed autoclave under elevated temperature and pressure conditions. This technique promotes controlled nucleation and crystal growth, leading to well-crystallized nanoparticles with uniform morphology and reduced agglomeration [24,25].

Hydrothermal synthesis is particularly effective for producing ZrO_2 nanostructures with controlled size and shape (Figure 3). Nevertheless, the requirement for high-pressure equipment and limited scalability restricts its large-scale industrial application [19].

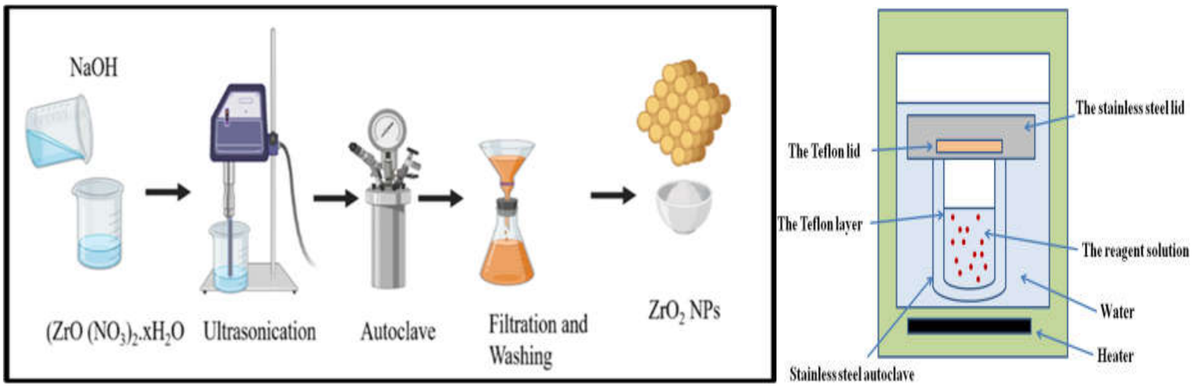


Figure 3. Conceptual diagram of hydrothermal synthesis of ZrO_2 nanomaterials in a sealed autoclave.

4.3 Co-precipitation Method

In the co-precipitation method, aqueous zirconium salt solutions are reacted with alkaline precipitants such as NH_4OH or NaOH, resulting in the formation of zirconium hydroxide precipitates. These precipitates are subsequently filtered, dried, and calcined to obtain ZrO_2 nanoparticles [24,26].

This method is simple, cost-effective, and suitable for large-scale synthesis (Figure 4). However, it often suffers from particle agglomeration and limited control over particle size distribution, which may negatively affect photocatalytic performance [19].

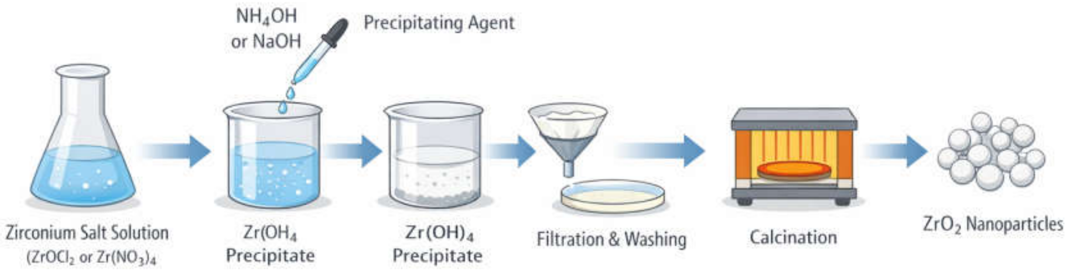


Figure 4. Schematic representation of the co-precipitation method for ZrO_2 nanoparticle synthesis.

4.4 Combustion Method

The combustion method is based on a rapid, self-sustaining exothermic reaction between metal precursors and suitable fuels. This process leads to the formation of ZrO_2 nanoparticles within a short reaction time [20].

Combustion synthesis is attractive due to its simplicity, fast processing, and ability to produce highly crystalline materials (Figure 5). However, controlling particle morphology and avoiding impurity formation remain significant challenges associated with this method [21].

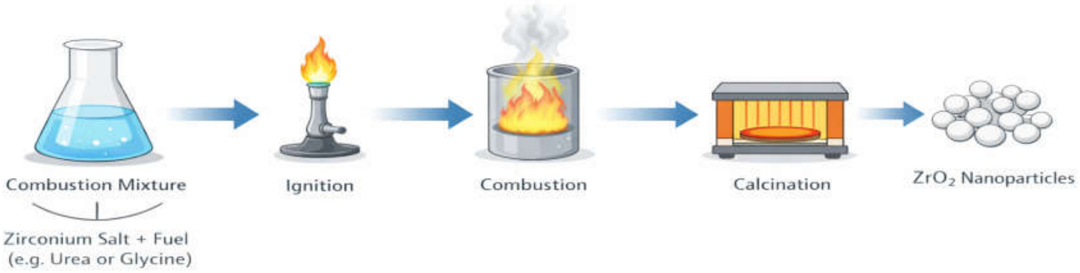


Figure 5. Illustrative diagram of the combustion synthesis route for ZrO_2 nanomaterials.

5. Dye Degradation Mechanism Using ZrO_2 Nanomaterials

The photocatalytic degradation of organic dyes over ZrO_2 nanomaterials proceeds through a sequence of light-induced redox reactions occurring on the catalyst surface [4–7].

5.1 Photogeneration of Charge Carriers

Upon irradiation with photons having energy equal to or greater than the band gap of ZrO_2, electrons in the valence band are excited to the conduction band, generating electron–hole pairs:

$$ZrO_2 + h\nu \rightarrow e^-(CB) + h^+(VB)$$

These photogenerated charge carriers form the basis for subsequent redox reactions [5,6].

5.2 Formation of Reactive Oxygen Species

The excited electrons and holes migrate to the surface of the ZrO_2 photocatalyst, where they participate in oxidation and reduction reactions. Electrons reduce dissolved oxygen molecules to form superoxide radicals ($\bullet O_2^-$), while holes oxidize water or hydroxide ions to generate hydroxyl radicals ($\bullet OH$). These reactive oxygen species possess strong oxidative potential and are primarily responsible for dye degradation [5,7].

5.3 Degradation of Dye Molecules

The generated reactive radicals attack dye molecules adsorbed on the catalyst surface, breaking complex aromatic structures into smaller intermediates (Figure 6). These intermediates undergo further oxidation reactions, ultimately leading to complete mineralisation into carbon dioxide, water, and inorganic ions [27].

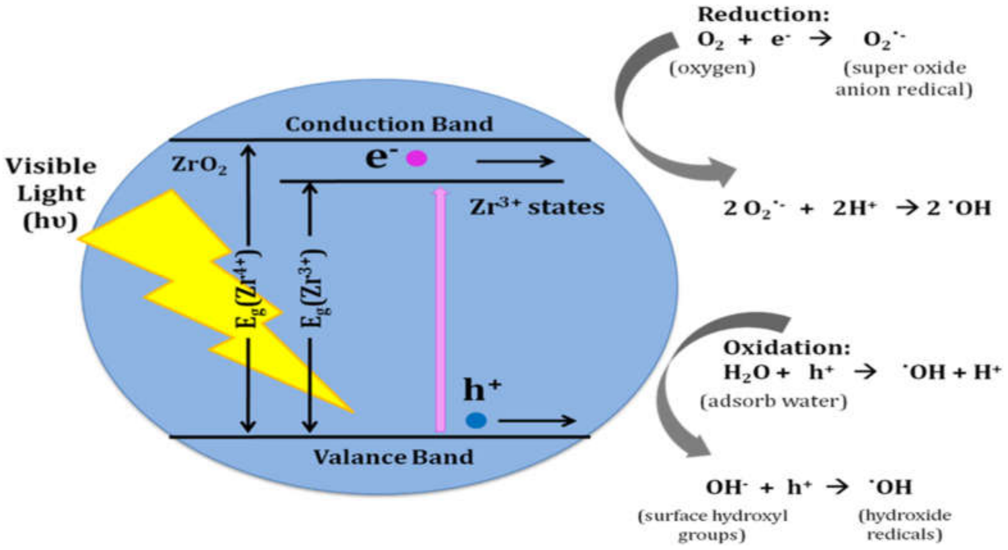


Figure 6. Schematic illustration of the photocatalytic dye degradation mechanism over ZrO_2 nanomaterials.

5.4 Effect of Material Modification

Material modification strategies such as elemental doping and composite formation play a critical role in enhancing the photocatalytic performance of ZrO_2. These approaches reduce electron–hole recombination, improve visible-light absorption, and facilitate efficient charge separation [35,40]. Consequently, modified ZrO_2-based systems generally exhibit significantly higher dye degradation efficiency compared to pristine ZrO_2 [19].

Comparison Table 1: Synthesis Methods of ZrO_2 Nanomaterials

Synthesis method	Key features	Advantages	Limitations	Typical photocatalytic relevance	References
Sol–gel	Hydrolysis and condensation of zirconium precursors followed by calcination	Excellent control over particle size and composition; high purity; low synthesis temperature	Longer processing time; use of organic solvents	Produces homogeneous ZrO_2 with high surface area, suitable for controlled photocatalytic studies	[21,22]
Hydrothermal	Crystallization under high temperature and pressure in a sealed autoclave	Well-crystallized nanoparticles; controlled morphology; low agglomeration	High-pressure equipment; limited scalability	Enhances crystallinity and charge transport, improving photocatalytic efficiency	[19,24]
Co-precipitation	Chemical precipitation using alkaline agents (e.g., NH_4OH, NaOH)	Simple, cost-effective; suitable for large-scale synthesis	Particle agglomeration; poor size control	Widely used for bulk synthesis, though surface modification is often required	[19,24]

Combustion	Rapid exothermic reaction between metal precursors and fuels	Fast synthesis; high crystallinity	Difficult morphology control; possible impurity formation	Useful for quick preparation of crystalline ZrO_2 but less control over surface properties	[20,21]

6. ZrO_2-Based Nanomaterials for Dye Degradation

ZrO_2-based nanomaterials have been widely explored as photocatalysts for the degradation of organic dyes owing to their excellent chemical stability, strong oxidative capability, and high resistance to photo corrosion [38,39]. Nevertheless, the intrinsic photocatalytic performance of ZrO_2 is strongly influenced by material design and structural modification [38]. Based on composition and modification strategies, ZrO_2 photocatalysts are generally classified into pristine ZrO_2, doped ZrO_2, and ZrO_2-based composite systems [19,21].

6.1 Pristine ZrO_2 Nanomaterials

Pristine ZrO_2 nanomaterials exhibit photocatalytic activity predominantly under ultraviolet light irradiation due to their wide band gap [39]. Numerous studies have reported the successful degradation of commonly used organic dyes, such as methylene blue, methyl orange, rhodamine B, and Congo red, using pure ZrO_2 nanostructures synthesized through sol–gel, hydrothermal, and co-precipitation methods [22–25].

The photocatalytic efficiency of pure ZrO_2 is governed by several key factors, including crystal structure, particle size, surface area, and the availability of surface hydroxyl groups [20]. In particular, the tetragonal phase of ZrO_2 often demonstrates superior photocatalytic activity compared to the monoclinic phase, primarily due to its higher surface energy and improved charge transport characteristics (Figure 7) [8,20]. However, despite these advantages, pristine ZrO_2 suffers from limited visible-light absorption and rapid recombination of photogenerated electron–hole pairs, which significantly restrict its application in solar-driven photocatalytic processes [19].

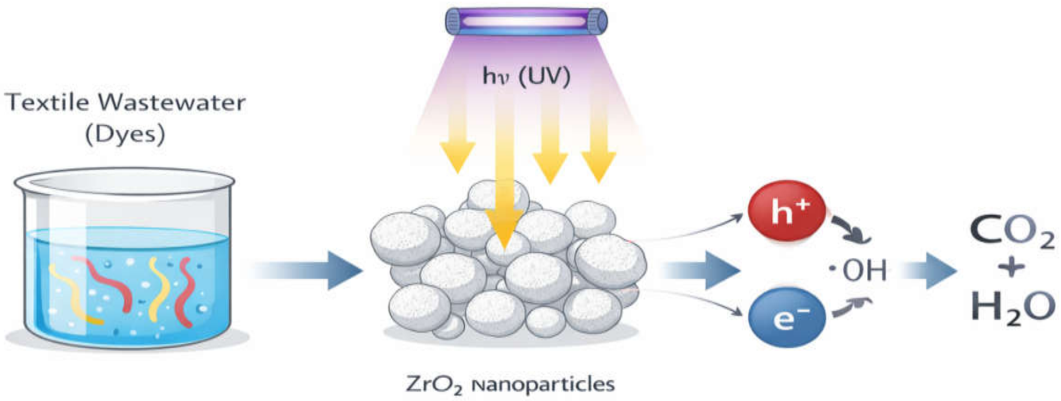


Figure 7. Illustrative representation of pristine ZrO_2 nanomaterials used for UV-driven photocatalytic dye degradation.

6.2 Doped ZrO_2 Nanomaterials

To overcome the inherent limitations of pristine ZrO_2, doping with suitable metal or non-metal elements has been extensively investigated [24,26]. Doping introduces defect states or impurity levels within the band structure, thereby enhancing light absorption and suppressing charge carrier recombination [26,21].

6.2.1 Metal-Doped ZrO_2

Metal doping involves the incorporation of transition metal ions such as Fe, Co, Ni, Cu, and Mn, as well as rare-earth ions including Ce and La, into the ZrO_2 lattice [24–28]. These dopants act as electron trapping centers (Figure 8), effectively reducing the recombination rate of electron–hole pairs and narrowing the effective band gap [24,25]. As a result, metal-doped ZrO_2 photocatalysts exhibit enhanced photocatalytic degradation efficiency under both ultraviolet and visible-light irradiation when compared to undoped ZrO_2 [26,28,19].

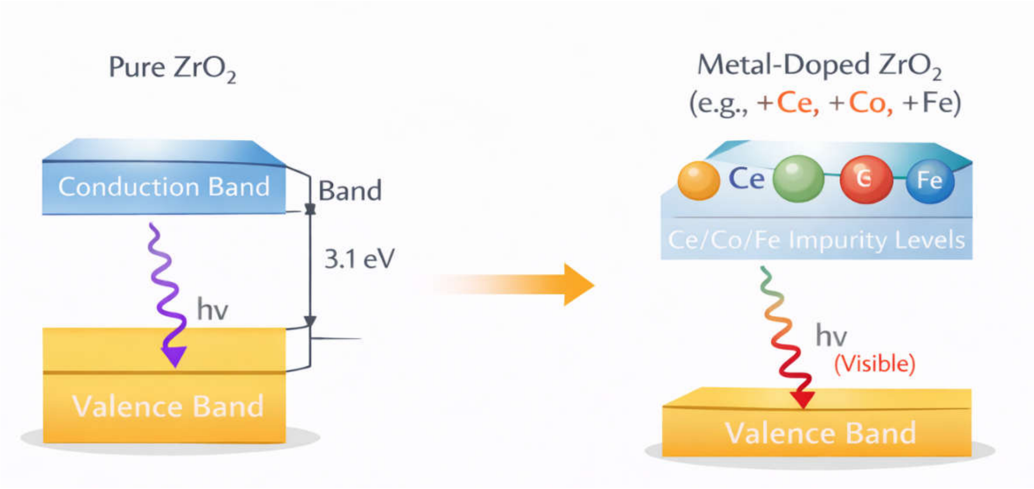


Figure 8. Band structure modification of ZrO_2 through metal doping for visible-light-driven photocatalysis

6.2.2 Non-Metal-Doped ZrO_2

Non-metal doping using elements such as nitrogen, sulfur, carbon, and fluorine has also gained significant attention. These dopants modify the electronic structure of ZrO_2 by introducing localized energy states near the valence band, thereby enabling visible-light excitation (Figure 9) [26]. Non-metal-doped ZrO_2 systems are particularly attractive due to their relatively low cost, minimal risk of metal ion leaching, and improved environmental compatibility [19,29]. Such materials have demonstrated promising photocatalytic performance under visible-light irradiation when compared to pristine ZrO_2 [19,21,26].

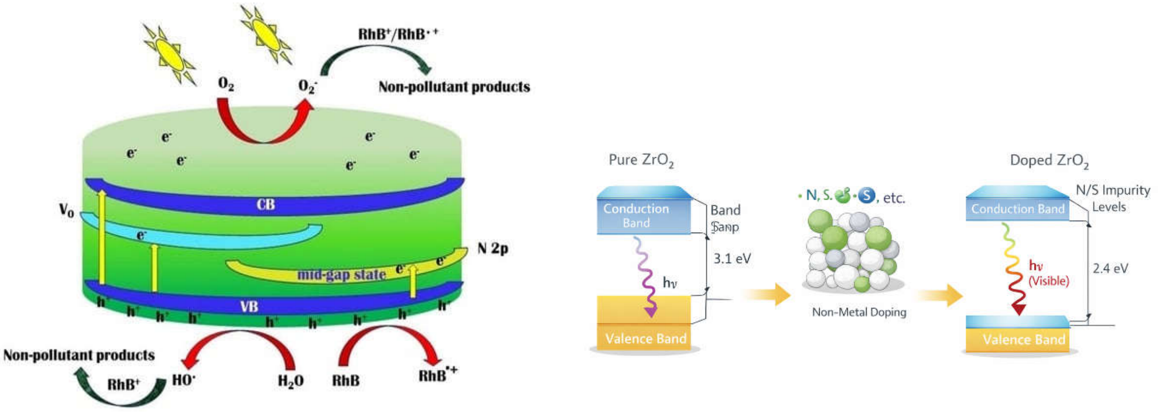


Figure 9. Band structure modification of ZrO_2 through non-metal doping for visible-light-driven photocatalysis.

6.3 ZrO_2-Based Composite Photocatalysts

The construction of ZrO_2-based composite photocatalysts represents one of the most effective approaches for improving dye degradation efficiency [27-30]. In such systems, ZrO_2 is coupled with other functional materials to form heterojunctions that promote efficient charge separation and extended light absorption [30].

6.3.1 ZrO_2–Metal Oxide Composites

ZrO_2 has been successfully combined with various metal oxides, including TiO_2, ZnO, SnO_2, and Fe_2O_3, to form heterojunction photocatalysts (Figure 10,11) [31,32]. These composite systems suppress electron–hole recombination, enhance interfacial charge transfer, and broaden the light absorption range [27-30]. Consequently, ZrO_2-metal oxide composites often exhibit significantly higher photocatalytic activity than their individual components [31,32].

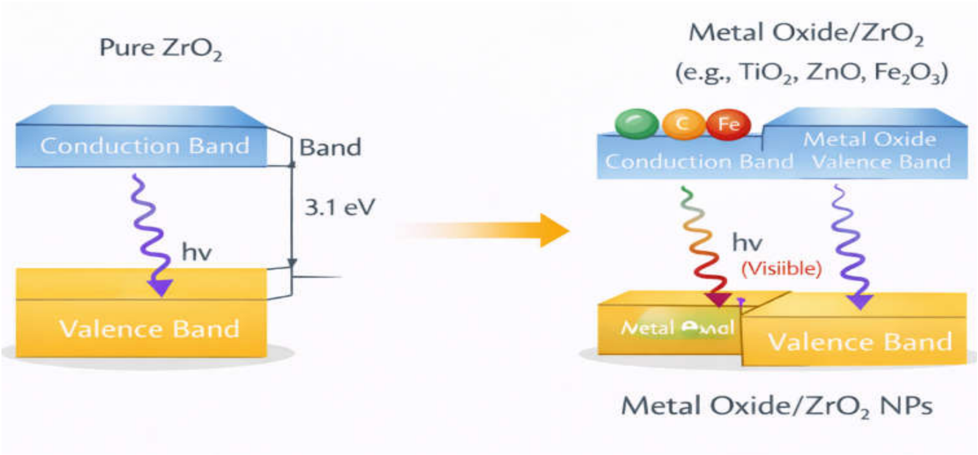


Figure 10. Band structure Modification ZrO_2 through heterojunction formation with metal oxide for visible-light driven photocatalysis.

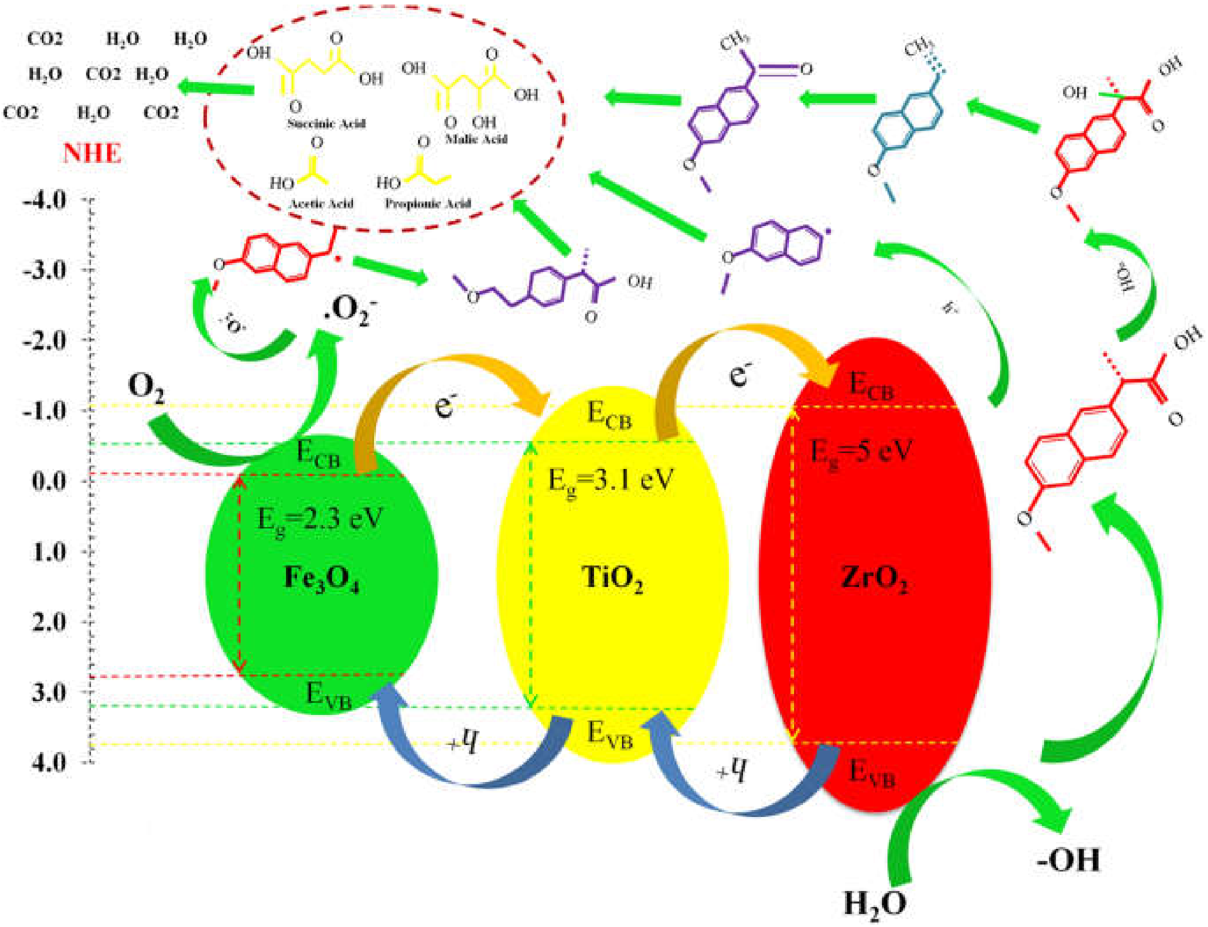


Figure 11. Heterojunction formation in ZrO_2–metal oxide composite photocatalysts for enhanced dye degradation.

6.3.2 ZrO_2–Carbon-Based Composites

Carbon-based materials such as graphene oxide, reduced graphene oxide, and carbon nanotubes have also been integrated with ZrO_2 to improve photocatalytic performance [28,33]. These materials serve as efficient electron acceptors and conductive pathways (Figure 12), facilitating rapid charge transport while providing additional adsorption sites for dye molecules [28]. As a result, ZrO_2–carbon-based composites demonstrate superior photocatalytic activity, particularly under visible-light irradiation [28,33].

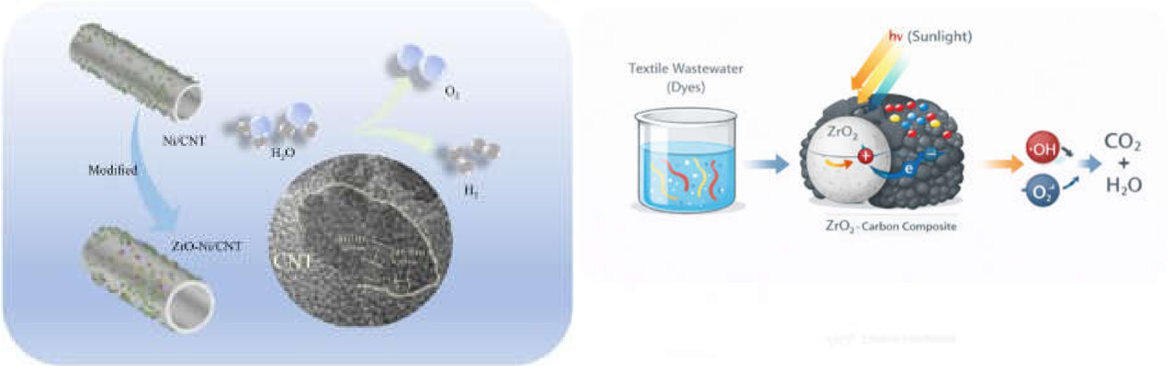


Figure 12. Schematic illustration of charge transfer and dye adsorption in ZrO_2–carbon-based composite photocatalysts.

6.4 Comparative Performance of ZrO_2-Based Photocatalysts

Overall, doped and composite ZrO_2-based photocatalysts consistently outperform pristine ZrO_2due to improved light harvesting, efficient charge separation, and enhanced surface reactivity [19,27]. However, practical considerations such as synthesis complexity, production cost, and long-term structural stability must be carefully evaluated to develop efficient and scalable ZrO_2-based photocatalysts for real-world wastewater treatment applications [27].

As summarized in Table 1, pristine ZrO_2 shows photocatalytic activity predominantly under ultraviolet irradiation, which can be attributed to its wide band gap [8,11,23]. In contrast, both doping and composite formation markedly improve photocatalytic performance by extending light absorption into the visible region and reducing the recombination of photogenerated charge carriers [22,24,33]. Among the various modification strategies, ZrO_2-based composite systems exhibit the most significant enhancement in dye degradation efficiency. In particular, composites formed with TiO_2 and carbon-based materials demonstrate superior photocatalytic activity owing to efficient interfacial charge transfer, improved light harvesting, and enhanced surface adsorption of dye molecules [30,35].

Table 1. Comparison of ZrO_2-Based Photocatalysts for Dye Degradation

Type of photocatalyst	Synthesis method	Target dye	Light source	Key performance	Major advantage	Limitation	References
Pure ZrO_2 nanoparticles	Sol–gel	Methylene blue	UV	~70–85% degradation in 60–120 min	High chemical and thermal stability	Wide band gap, UV-active only	[11,23,25]
Pure ZrO_2 nanoparticles	Hydrothermal	Methyl orange	UV	Moderate degradation efficiency	High crystallinity, low defects	Fast e^-–h^+ recombination	[12,24,25]
Fe-doped ZrO_2	Co-precipitation	Rhodamine B	UV/Visible	Enhanced degradation compared to pure ZrO_2	Reduced band gap, improved charge separation	Possible metal ion leaching	[9,29,31]
Ce-doped ZrO_2	Sol–gel	Congo red	Visible	High degradation efficiency under visible light	Oxygen vacancy formation, improved ROS generation	Complex synthesis control	[31,28]
N-doped ZrO_2	Sol–gel	Methylene blue	Visible	Improved visible-light activity	Metal-free, eco-friendly	Lower stability than metal-doped systems	[28,30]
ZrO_2–TiO_2 composite	Sol–gel	Methyl orange	UV/Visible	>90% degradation in shorter time	Efficient heterojunction formation	Phase compatibility issues	[33,35]

7. Challenges and Future Scope of ZrO_2-Based Photocatalysts

ZrO_2–ZnO composite	Hydrothermal	Rhodamine B	UV	Higher activity than individual oxides	Enhanced interfacial charge transfer	Limited visible-light response	[19]
ZrO_2–graphene oxide composite	Hydrothermal	Methylene blue	Visible	Rapid and efficient degradation	Excellent electron transport, high adsorption	High cost of carbon materials	[20,34]
ZrO_2–CNT composite	Sol–gel	Congo red	Visible	Improved reaction kinetics	Suppressed recombination	Difficult large-scale synthesis	[20,34]

Despite the encouraging results reported for ZrO_2-based nanomaterials in photocatalytic dye degradation, several scientific and technological challenges still limit their large-scale and practical implementation [21,27]. Addressing these issues is essential for translating laboratory-scale successes into real-world wastewater treatment applications.

7.1 Current Challenges

7.1.1 Wide band gap and limited visible-light activity

ZrO_2 is intrinsically a wide band gap semiconductor, which restricts its photo response primarily to the ultraviolet region [8,11,23]. Since ultraviolet light represents only a small fraction of the solar spectrum, this significantly limits the efficiency of ZrO_2-based photocatalysts under natural sunlight [21].

7.1.2 Rapid electron–hole recombination

The fast recombination of photogenerated charge carriers remains a major drawback, as it reduces the availability of reactive oxygen species required for effective dye degradation, thereby lowering overall photocatalytic efficiency [22,24].

7.1.3 Stability and reusability concerns

Although pristine ZrO_2 exhibits excellent chemical stability, doped and composite systems may experience dopant leaching, interfacial degradation, or gradual loss of activity during repeated photocatalytic cycles, adversely affecting long-term performance and practical usability [20,21].

7.1.4 Nanoparticle agglomeration

At the nanoscale, ZrO_2 particles tend to agglomerate during synthesis and photocatalytic operation, leading to a reduction in surface area and a decrease in the number of accessible active sites [11,18].

7.1.5 Scalability and economic limitations

Many high-performance ZrO_2-based photocatalysts rely on complex synthesis procedures, costly precursors, or carbon-based additives, which pose challenges for large-scale production and commercial viability [20,21].

7.2 Future Scope and Research Directions

7.2.1 Advanced band gap engineering

Future studies should focus on rational band gap tuning through co-doping strategies, defect engineering, and phase-controlled synthesis to enable efficient visible-light-driven photocatalysis [22,24,33].

7.2.2 Design of efficient heterojunction architectures

The development of ZrO_2-based heterostructures with well-matched band alignment can significantly enhance charge separation and prolong charge carrier lifetimes, with interface engineering playing a crucial role in next-generation photocatalyst design [30,33].

7.2.3 Solar-driven and real wastewater applications

Most reported studies are based on synthetic dye solutions under controlled laboratory conditions. Future research should emphasize solar-driven photocatalytic systems, treatment of real industrial wastewater, and performance evaluation under realistic environmental conditions [18,21].

7.2.4 Improved catalyst recovery and reuse

The fabrication of magnetically separable or immobilized ZrO_2-based photocatalysts offers a promising route to simplify catalyst recovery, minimize material loss, and improve reusability [20,21].

7.2.5 Environmental safety and toxicity assessment

Comprehensive investigations into the environmental fate, toxicity, and ecological impact of ZrO_2 nanomaterials are essential before their large-scale deployment [20,21].

7.2.6 Integration with hybrid treatment technologies

Combining ZrO_2 based photocatalysis with complementary techniques such as adsorption, membrane filtration, or biological treatment may lead to highly efficient and sustainable hybrid wastewater treatment systems [21].

8. Conclusion

This review has systematically examined recent advances in ZrO_2-based nanomaterials for the photocatalytic degradation of organic dyes, with emphasis on their physicochemical properties, synthesis strategies, photocatalytic mechanisms, and application performance. ZrO_2nanomaterials have emerged as promising photocatalysts due to their excellent chemical and thermal stability, non-toxic nature, and strong oxidative capability. However, the intrinsically wide band gap of ZrO_2 limits its photoactivity mainly to the ultraviolet region, thereby restricting its effectiveness under solar irradiation. Various synthesis methods, including sol–gel, hydrothermal, co-precipitation, and combustion techniques, play a critical role in controlling the crystal structure, particle size, surface area, and phase stability of ZrO_2 nanomaterials, which directly influence photocatalytic performance. Furthermore, material modification approaches such as metal and non-metal doping, as well as the construction of ZrO_2-based composite and heterojunction systems, have proven effective in extending visible-light absorption, suppressing electron–hole recombination, and enhancing dye degradation efficiency. Comparative analysis of reported studies clearly indicates that doped and composite ZrO_2 systems outperform pristine ZrO_2, particularly under visible-light irradiation, due to improved charge separation and enhanced light harvesting. In particular, ZrO_2-based composites with other metal oxides and carbon materials demonstrate superior photocatalytic activity, stability, and reusability, making them strong candidates for wastewater treatment applications. Despite these significant advancements, challenges related to limited solar utilization, catalyst recovery, long-term stability, and scalability remain unresolved. Future research efforts should focus on rational material design, advanced band gap engineering, development of solar-driven systems, and evaluation under real wastewater conditions. Overall, ZrO_2-based nanomaterials hold considerable potential for sustainable environmental remediation, and continued research is expected to accelerate their practical implementation in large-scale dye-contaminated wastewater treatment.

References

[1] Hoffmann MR, Martin ST, Choi W, Bahnemann DW. Environmental applications of semiconductor photocatalysis. *Chem Rev*. 1995;95:69–96.

[2] Herrmann JM. Heterogeneous photocatalysis: fundamentals and applications to the removal of aqueous pollutants. *Catal Today*. 1999;53:115–129.

[3] Chong MN, Jin B, Chow CWK, Saint C. Recent developments in photocatalytic water treatment technology: a review. *Water Res*. 2010;44:2997–3027.

[4] Pelaez M, Nolan NT, Pillai SC, et al. A review on the visible light active photocatalysts for environmental applications. *Appl Catal B*. 2012;125:331–349.

[5] Nosaka Y, Nosaka AY. Generation and detection of reactive oxygen species in photocatalysis. *Chem Rev*. 2017;117:11302–11336.

[6] Kamat PV. Manipulation of charge transfer across semiconductor interfaces. *J Phys Chem Lett*. 2012;3:663–672.

[7] Ahmed S, Rasul MG, Brown R, Hashib MA. Influence of parameters on heterogeneous photocatalytic degradation of dyes. *J Environ Manag*. 2011;92:311–330.

[8] Chevalier J, Gremillard L, Virkar AV. The tetragonal–monoclinic transformation in zirconia. *J Am Ceram Soc*. 2009;92:1901–1920.

[9] Navío JA, Hidalgo MC, Colón G, Botta SG, Litter MI. Preparation and characterization of ZrO_2 and Fe-doped ZrO_2 photocatalysts. *Langmuir*. 2001;17:202–210.

[10] Xu Y, Schoonen MAA. The absolute energy positions of conduction and valence bands of semiconductors. *Am Mineral*. 2000;85:543–556.

[11] Wang S, Li H, Xie S, Liu S, Xu L. Physical and photocatalytic properties of ZrO_2 nanoparticles. *J Photochem Photobiol A*. 2006;181:33–39.

[12] Sreethawong T, Yoshikawa S. Comparative investigation on photocatalytic activity of nanocrystalline ZrO_2. *J Mol Catal A*. 2005;235:1–11.

[13] Ruiz-Santoyo V, et al. Structural and optical characterization of TiO_2–ZrO_2 nanocomposites. *Catalysts*. 2021;11:980.

[14] Zare MH, et al. $ZrO_2/TiO_2/Fe_3O_4$ ternary nanocomposites with enhanced photocatalytic performance. *Sci Rep*. 2022;12:18465.

[15] Diaz-Uribe C, et al. Role of oxygen vacancies in ZrO_2-based photocatalysts. *Mater Chem Phys*. 2024;307:127891.

[16] Acosta-Silva YJ, et al. Band gap tuning and photocatalytic performance of ZrO_2 thin films. *Coatings*. 2024;14:312.

[17] Keerthana SP, et al. PL studies of Nd-doped ZrO_2 correlated with photocatalytic activity. *Mater Today Proc*. 2022;62:4528–4535.

[18] Sharma S, et al. Mesoporous ZrO_2 nanoparticles for sunlight-driven dye degradation. *Environ Nanotechnol Monit Manag*. 2023;20:100844.

[19] Singh R, et al. ZrO_2-based nanomaterials for environmental remediation. J Environ Chem Eng. 2023;11:109234.

[20] Ahmed MA, El-Katori EE. ZrO_2 nanoparticles and photocatalytic applications. J Photochem Photobiol A. 2013;256:47–55.

[**21**] Kumar SG, Devi LG. Review on modified semiconductor photocatalysis. J Phys Chem A. 2011;115:13211–13241.

[22] Aljawrneh B. Synthesis of ZrO_2 nanoparticles for photocatalytic degradation of methylene blue. *J Environ Chem Eng*. 2024;12:110215.

[23] Seyrek M. Photocatalytic degradation of automotive dye wastewater using ZrO_2 nanoparticles. *Environ Technol*. 2023;44:2150–2162.

[24] Navío JA, Colón G, Macías M, Hidalgo MC. Iron-doped ZrO_2 powders as photocatalysts. *Appl Catal A*. 1999;177:111–120.

[25] Reddy BM, Khan A, Lakshmanan P. Structural characterization of CeO_2–ZrO_2 mixed oxides. *J Phys Chem B*. 2005;109:3355–3363.

[26] Wang J, Yang P, Wang X, Li C. Nitrogen-doped ZrO_2 photocatalysts under visible light. *J Alloys Compd*. 2013;574:337–343.

[27] Khan S, et al. Photocatalytic dye degradation from textile wastewater: a review. *ACS Omega*. 2024;9:11450–11472.

[28] Zhang N, Yang MQ, Tang ZR, Xu YJ. Graphene-based photocatalysts. *ACS Nano*. 2013;7:3279–3287.

[29] Li X, Chen G, Yang L. Visible-light-driven N-doped ZrO_2 nanoparticles. *Appl Surf Sci*. 2014;308:264–270.

[30] Li Y, et al. Semiconductor heterojunctions for visible-light photocatalysis. *Appl Catal B*. 2020;268:118741.

[31] Yu J, Zhou M, Cheng B, Zhao X. ZrO_2–TiO_2 composite photocatalysts. *J Mol Catal A*. 2006;246:176–184.

[32] Al-Harbi LM, et al. ZrO_2–ZnO heterojunctions for photocatalytic dye removal. *Ceram Int*. 2020;46:18265–18275.

[33] Wang H, et al. Carbon-based semiconductor photocatalysts for water treatment. *Chem Eng J*. 2021;405:126610.

[34] Zare MH, et al. Magnetically recoverable ZrO_2-based photocatalysts. *J Hazard Mater*. 2021;416:125873.

[35] Zhou Y, et al. Recent advances in magnetic photocatalysts. *J Clean Prod*. 2022;334:130168.