INGENIERÍA E INVESTIGACIÓN VOL. 46 No. 1, 2026 (e120219)

DOI: http://doi.org/10.15446/ing.investig.120219

Research Article/Chemical, Food, and Environmental Engineering

Advances in ZrO_2 Photocatalysis for Dye Degradation: A Review

Avances en la fotocatálisis basada en el ZrO_2 para la degradación de colorantes: una revisión

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ABSTRACT

Nanoscience has driven significant advances in functional materials engineering. In this context, zirconium oxide (ZrO_2) has been widely explored due to its physicochemical properties, with applications in catalysis, sensors, adsorption, and biomedicine. This review aimed to analyze recent developments in the synthesis and modification of ZrO_2 nanoparticles to improve their photocatalytic efficiency, especially in the degradation of organic pollutants present in aqueous solutions. A systematic literature search was conducted in databases such as Scopus, Web of Science, and Google Scholar, following the PRISMA protocol. Studies published between 2010 and 2023 were selected. The three crystalline phases of ZrO_2, their optical properties, and the effects of synthesis on their catalytic performance were described. The mechanisms of generation and separation of e^-/h^+ pairs and their relationship with the formation of oxidizing radicals were summarized. Results indicated that the efficiency of ZrO_2 improves significantly through strategies such as metal doping, coupling with semiconductors, and combination with Anderson-type polyoxometalates (POMs), *i.e.*, discrete anionic metal-oxo cluster with redox activity that can act as electron reservoirs, promoting charge separation and reactive-species formation during photocatalysis. The potential of thin films as support for hybrid materials was highlighted, as they increase the active surface area and structural stability. It was concluded that the ZrO_2-POMs combination represents a promising pathway for environmental remediation applications, although experimental studies are still required to validate its efficiency under real conditions.

Keywords: photocatalysis, adsorption, ZrO_2, polyoxometalates (POMs), catalytic efficiency.

RESUMEN

La nanociencia ha impulsado avances significativos en la ingeniería de materiales funcionales. En este contexto, el óxido de zirconio (ZrO_2) ha sido ampliamente explorado por sus propiedades fisicoquímicas, para el desarrollo de aplicaciones en catálisis, sensores, adsorción y biomedicina. La presente revisión tuvo como objetivo analizar los desarrollos recientes en la síntesis y modificación de nanopartículas de ZrO_2 orientadas a mejorar su eficiencia fotocatalítica, especialmente en la degradación de contaminantes orgánicos presentes en soluciones acuosas. Se realizó una búsqueda sistemática de literatura en bases de datos como Scopus, Web of Science y Google Scholar, siguiendo el protocolo PRISMA. Se seleccionaron estudios publicados entre 2010 y 2023. Se describieron las tres fases cristalinas del ZrO_2, sus propiedades ópticas, y los efectos de la síntesis sobre su rendimiento catalítico. Se resumieron los mecanismos de generación y separación de pares e^-/h^+ y su relación con la formación de radicales oxidantes. Los resultados indicaron que la eficiencia del ZrO_2 mejora significativamente mediante estrategias como dopado metálico, acoplamiento con semiconductores y combinación con polioxometalatos tipo Anderson (POMs), es decir, clústeres aniónicos metal-oxo con actividad redox que pueden actuar como reservorios de electrones, favoreciendo la separación de cargas y formación de especies reactivas en la fotocatálisis. Se destacó el potencial de las películas delgadas como soporte para materiales híbridos, al incrementar la superficie activa y la estabilidad estructural. Se concluyó que la combinación ZrO_2–POMs representa una vía prometedora para aplicaciones de remediación ambiental, aunque aún se requieren estudios experimentales que validen su eficiencia en condiciones reales.

Palabras clave: fotocatálisis, adsorción, ZrO_2, polioxometalatos (POMs), eficiencia catalítica.

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Received: May 5th 2025
Accepted: January 13th 2026

Introduction

According to the *World Population Prospects* report published by the United Nations on November 15, 2022, the global population reached a historic milestone of approximately 8 billion people [1]. This growth is primarily attributed to increased human life expectancy; however, it has also led to severe environmental consequences resulting from unsustainable urbanization processes, industrial expansion, and intensified agricultural production. These trends have exponentially increased the generation and emission of pollutants into the environment [2], giving rise to the concept of the Anthropocene as a period of substantial transformation in Earth's biogeochemical cycles [3, 4, 5].

To address environmental pollution, more efficient treatment methods have been proposed [6, 7, 8]. Among these, Advanced Oxidation Processes (AOPs) have emerged as promising alternatives due to their ability to operate at ambient temperature and pressure. AOPs rely on the *in situ* generation of reactive oxygen species (ROS) on the catalyst surface under specific conditions, which act as oxidizing agents capable of degrading recalcitrant contaminants [9].

Among AOPs, heterogeneous photocatalysis has proven highly effective for the remediation of polluted waters [10]. In this process, a semiconductor is activated by photons with energy equal to or greater than its band gap (Eg), promoting the generation of reactive species with high oxidizing power, capable of degrading complex organic compounds [11, 12].

Metal oxides such as TiO_2 and ZnO have been extensively studied for their photocatalytic properties [13]. However, ZrO_2 (IV) has emerged as an outstanding alternative due to its photophysical and photochemical versatility, which can be modulated through eco-friendly synthesis methods, phase stabilization strategies, and controlled precursors and pretreatment conditions [14]. A notable feature of ZrO_2 is its unique ability to simultaneously exhibit acidic, basic, oxidizing, and reducing properties [15]. Structurally, it presents high density, thermal and fracture resistance, low thermal conductivity, photochemical stability, and a high refractive index [16].

From an optical standpoint, ZrO_2 is a wide-band-gap semiconductor characterized by transparency in the visible and infrared regions of the spectrum and low photon energy, which minimizes the probability of non-radiative transitions by multiphoton relaxation [17]. Additionally, it exhibits a high density of oxygen vacancies on its surface associated with its ion-exchange capacity and redox properties [18].

The optical energy of the photons absorbed by ZrO_2 strongly depends on its crystalline phase. By modifying its surface, light absorption and charge separation are improved, enhancing its photocatalytic capability; however, its stability at room temperature is largely determined by the synthesis method employed [14].

This article presents a review of recent advances in the synthesis and modification of zirconium dioxide nanoparticles (ZrO_2 NPs), aimed at optimizing their optical, structural, and thermal properties for dye photodegradation applications. Various approaches are addressed: including (i) coupling with other semiconductors, (ii) the formation of hybrid or ternary systems, and (iii) integration with polyoxometalates. All of which seek to increase the density of oxygen vacancies, while also improving the efficiency of contaminant removal mechanisms. Likewise, the potential application of these materials in aqueous solutions treatment is discussed, particularly in combination with Anderson-type polyanionic species, considering their synergy with ZrO_2 as a means to enhance photocatalytic activity.

Methodology

The bibliographic review was conducted using specialized databases, including Web of Science, Google Scholar, and Scopus, following the PRISMA guidelines for systematic reviews and meta-analyses [79]. This review aimed to systematically identify relevant studies on ZrO_2-based photocatalyst by applying to titles, abstracts, and keywords the following search terms: *Zirconium* OR *Zircon* OR *ZrO_2* AND *Photocatalysis* AND *removal* OR *adsorption** OR *eliminat** OR *treatment**.

The period considered ranged from January 2010 to January 2023, as shown in Fig. 1. Only experimental and computational studies published in English were included. Articles focused exclusively on bulk ceramic materials, as well as commentaries, narrative reviews, and undergraduate theses, were excluded.

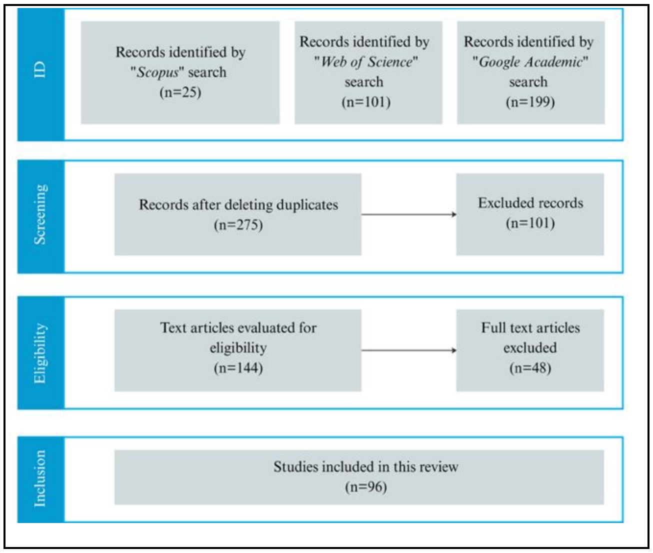

Figure 1. PRISMA methodology flowchart of the systematic review process. (2010-2023)
Source: Authors

The selected documents were managed using the bibliographic software VOSviewer for their relevance evaluation, as shown in Fig. 2. Titles and abstracts were analyzed according to the established inclusion criteria.

Photophysical and Photochemical Properties of ZrO_2

Zirconium (Zr) is naturally found as zircon ($ZrSiO_4$) and baddeleyite (ZrO_2), a byproduct of titanium purification [19]. Its natural abundance and physicochemical properties have enabled its applications in coagulants, catalysts, adsorbents, ceramics, and dental implants [15], [20], [21], [22], [23].

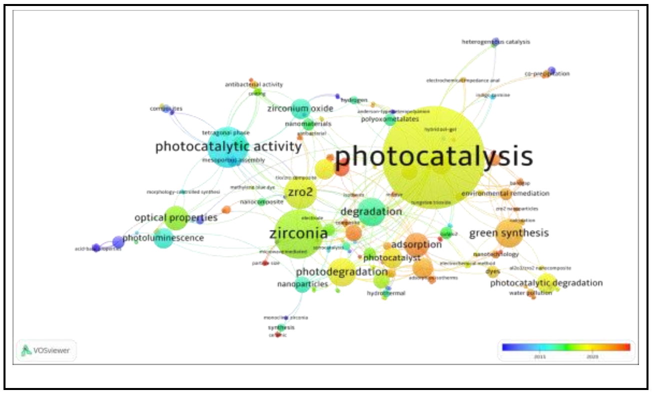

Figure 2. Keyword co-occurrence network diagram.
Source: Authors (created with VOSviewer)

Recently, ZrO_2 has attracted considerable interest due to its chemical stability, non-toxicity, and cost-effectiveness. It has been widely studied for dye and pollutant photodegradation [24], [25], [26], as well as for hydrogen production [27], [28], [29], although the latter application still requires further technological development.

ZrO_2 is generally described as a wide-bandgap n-type semiconductor; however, its apparent conductivity/type may vary depending on defect chemistry, oxygen vacancy concentration, and processing conditions. Its high band gap (~5.0 eV) restricts light absorption to the UV region (<4% of the solar spectrum) and promotes rapid e^-/h^+ recombination, thereby limiting its photocatalytic efficiency [30], as seen in Fig. 3.

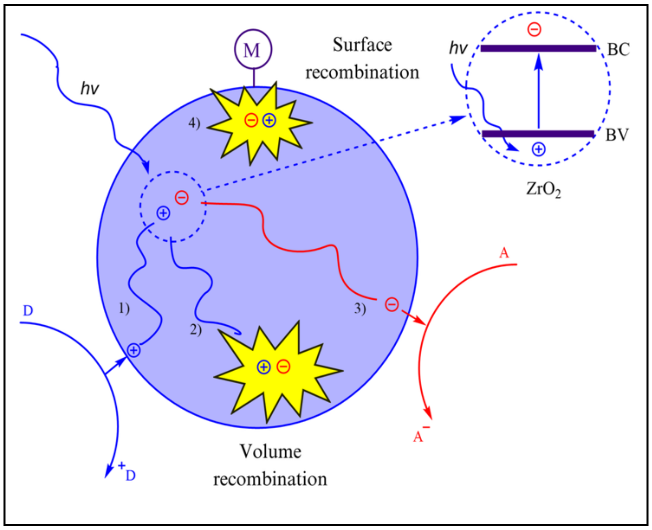

Figure 3. Schematic representation of the photoexcitation process in ZrO_2 and possible recombination pathways.
Source: Adapted from [1]

To extend its response into the visible spectrum, structural defects can be introduced through thermal and synthesis treatments [15], [32], which increase the specific surface area, improve adsorption [33], [34], and adjust electronic levels [35].

As demonstrated in [36], in Cu/ZrO_2 systems, defect-induced morphologies act as effective electron traps during the degradation of rhodamine B. Similarly, ZrO_{2}-x with a disordered lattice and reduced Eg (1.5 eV) was developed in [37], achieving good performance in RhB degradation and H_2 production under solar irradiation.

The limited efficiency of pure ZrO_2 has motivated coupling strategies with other materials in order to form heterojunctions that improve charge separation and extend absorption [13]. As reported in [38], a ternary nanocomposite, ZrO_2/polyaniline/phosphotungstic acid (PTA-Zr), exhibited effective degradation of methylene blue, p-*nitrophenol* (PNP) and 2,4-dichlorophenoxyacetic acid (2,4-D). Their strategy follows a Z-scheme type mechanism [39], which can be seen in Fig. 4.

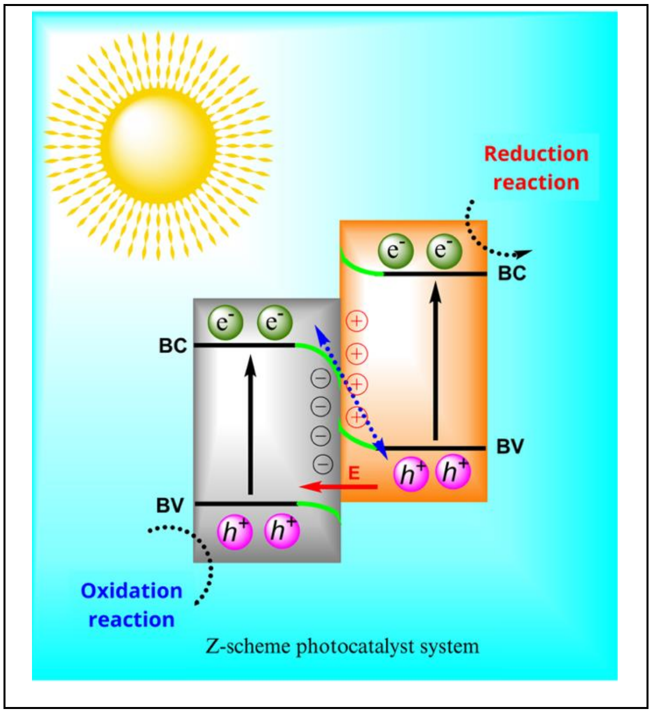

Figure 4. Schematic representation of the Z-scheme mechanism, understood as the coupling of two redox systems that absorb different wavelengths of light. A redox mediator facilitates electron transfer from the conduction band of the lower-energy semiconductor to the valence band of the higher-energy semiconductor.
Source: Adapted from [2]

Despite the growing number of studies, no comprehensive review has been identified focusing specifically on ZrO_2 thin films combined with Anderson-type polyoxometalates as a way to enhance its photocatalytic efficiency.

Background on ZrO_2 Photocatalysis

The optical activity of ZrO_2 depends on its absorption region, which can be classified as intrinsic (hv > 5.0 eV) or extrinsic (hv < 5.0 eV). In the former, defects are generated by photoionization, whereas, in the latter, they occur by the formation of F- and V-type color centers, which directly affect the photophysical and photochemical mechanisms of the material [41].

F centers arise from electrons trapped in anion vacancies by neutral defects, while V centers are formed by trapping electrons in positively charged defects [40]. These defect structures influence the ability of ZrO_2 to absorb and emit light [40].

Thermal irradiation (≈900 °C) in a controlled atmosphere favors the creation of defects such as Zr^{3+}, cationic vacancies, and F/F^+ centers, promoting reduced states useful in photocatalysis through photochromism [34], [41].

In [42], different synthesis routes of NP-ZrO_2 were compared in the degradation of methylene blue under UV light. The results indicated that the interaction between O_2 and oxygen vacancies or Zr^{3+} sites facilitates the generation of radicals, as described in Equation (1).

$$\begin{gathered}
ZrO_2 + hv \rightarrow h^+ + e^- \\
h^+ + e^- \rightarrow Energía \\
O_2 + F \rightarrow O_2^{\cdot -} + F^+ \\
Zr^{4+} + e^- \rightarrow Zr^{3+} \\
Zr^{3+} + O_2 \rightarrow Zr^{4+} + O_2^{\cdot -} \\
H_2O + h^+ \rightarrow H^+ + O_2^{\cdot -} \\
H^+ + O_2^{\cdot -} \rightarrow HO_2^{\cdot} \\
HO_2^{\cdot} + e^- + H^+ \rightarrow H_2O_2^{\cdot} \\
H_2O_2^{\cdot} \rightarrow \cdot OH + OH^- \\
O_2^{\cdot -} + AM \rightarrow Degradation \\
\cdot OH + AM \rightarrow Degradation
\end{gathered} \tag{1}$$

Source: Adapted from [3].

F centers transfer electrons to O_2, generating superoxide radicals ($O_2•^-$), which subsequently react with protons to form $HO_2•$, H_2O_2, and ultimately OH• radicals, responsible for dye degradation.

Current research focuses on optimizing the use of ZrO_2 in UV-visible light-activated reactions, employing sustainable synthesis routes for metallic nanomaterials with applications in photocatalysis, adsorption, and emerging processes [43].

Synthesis of ZrO_2 Nanostructures Applied in Photocatalysis

ZrO_2 can adopt three allotropic structures at atmospheric pressure: monoclinic (m-ZrO_2), tetragonal (t-ZrO_2), and cubic (c-ZrO_2), as shown in Fig. 5.

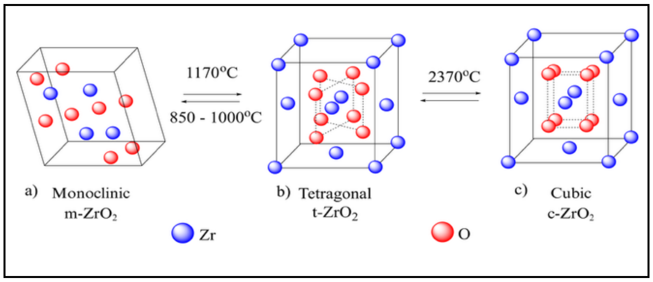

Figure 5. Schematic representation of crystal structures of ZrO_2 (a) monoclinic ZrO_2, (b) tetragonal ZrO_2 and (c) cubic ZrO_2.
Source: Adapted from [4]

The monoclinic phase (m-ZrO_2) is stable at room temperature, transforming into the tetragonal phase at 1170 °C and the cubic phase at 2370 °C. These transitions are reversible. The monoclinic structure, being less symmetrical and more defective, favors catalytic activity [45]. The tetragonal phase (t-ZrO_2) phase stands out for its redox capacity and optical stability, while the cubic phase forms only at high temperatures [46], [47], [48], as illustrated **in** Fig. 6.

Although a larger surface area typically implies greater adsorption, the adsorption coefficient also plays a critical role. As demonstrated in [5], despite having a low surface area, m-ZrO_2 performed better in the degradation of methyl orange than mixed phases. Furthermore, [6] highlighted that a mixture of m-ZrO_2/t-ZrO_2 phases with small particles improves methylene blue degradation

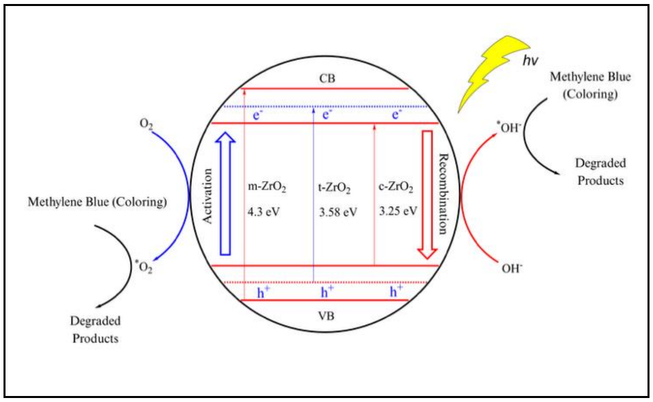

Figure 6. Schematic representation of the processes leading to the photocatalytic degradation of ZrO_2.
Source: Adapted from [5]

The photocatalytic efficiency of ZrO_2 depends on its crystallinity, size, and band gap, all of which are affected by synthesis conditions [7], [8]. Parameter such as pH, concentration, reaction temperature, and type of surfactant modulate its morphology and adsorption capacity [9], [10], [11], [12], [13], [14].

The sol-gel method enables precise control over the size and shape of NP-ZrO_2, operating at relatively low temperatures with homogeneous mixing at the atomic level [15]. Although xerogels are widely studied, ZrO_2 aerogels have been little explored [16].

Several studies have evaluated the impact of calcination and synthesis method on the structural and optical properties of ZrO_2 [7], [17], [18], [19], [20]. In [21], it was reported that annealing induces oxygen vacancies, modifying its photoluminescence. In [6], these changes were correlated to catalytic efficiency, using sol-gel synthesis and supercritical drying for the degradation of formic acid under UV.

Degradation of Organic Pollutants

Although ZrO_2 has a wide band gap, it has demonstrated efficiency in degrading dyes such as Eriochrome Black T [22] and Rhodamine B [23] under UV and visible light, respectively. The monoclinic phase exhibited higher activity than other phases, attributed to its crystal structure, oxygen vacancies, and hydroxylated surface [5]. Table I summarizes the photocatalytic performance reported for pure and modified ZrO_2-based materials in dye degradation under the experimental conditions of each study. Table II compiles the dopants and heterostructured architectures proposed in the selected literature corpus. pH also affects photocatalytic performance: under acidic conditions, ZrO_2 has a positive charge and degrades anionic dyes better due to the stability of oxidizing species such as H_2O_2 [24].

Table I. Photocatalytic activities of ZrO_2-based materials reported for dye degradation.

NP/ Ref	Eg (eV)	Size (nm)	Geometry	Range	Light source	Dye	Time (min)	Degradation(%)
ZrO_2/ [80]	3.78	17	Spherical	-	VIS	RY 160	120	94

ZrO_2/ [81]	4.9	15	Spherical	10-18	UV	Methylene Blue and Methyl Orange	240	91 69
ZrO_2/ [27]	5.44	19.93	Tetragonal	15-25	VIS	Methyl orange	90	68.4
ZrO_2 doped with Nd/ [82]	1.23	-	Agglomerate	-	VIS	Methylene Blue Rhodamine B	20 20	90 77
ZrO_2 doped with Mn/ [83]	4.96 - 2.43	-	Tetragonal	10.5 - 23.2	VIS	Methyl orange	100	83.7
ZrO_2 doped with Fe/ [84]	4.29	-	Tetragonal	18.78	VIS UV	Rhodamine B	150	100
ZrO_2 doped with Ag/ [85]	3.6	4.68	Spherical, monoclinic and tetragonal aggregates	15-20	VIS UV	Methylene Blue Methyl orange	160	91 99
ZrO_2 doped with Mg/ [86]	Varied	-	Spherical, tetragonal and hexagonal aggregates	-	UV	Rhodamine B	60	93
Carbon nanotubes/ ZrO_2/ [87]	2.6	-	-	23-87	VIS	Methylene Blue	120	90-94 87-96
Zn-ZrO_2 /[81]	3.96 3.99 3.97 4.01	79.56 98.78 54.86 67.43	-	-	sunlight	Rhodamine 6G	330	98 94
Pd/ ZrO_2 Pt/ZrO_2/[88]	-	-	-	100-700	VIS UV	Indigo carmine	120	97 95
Reduced graphene oxide-ZrO_2/ [89]	3.25	-	-	-	sunlight	Reactive Blue 4	120	93

Table II. Compiles the dopants and heterostructured architectures proposed in the selected literature corpus (PRISMA 2010-2023).

Modification type	**Subtype**	**Examples (recommender notation)**	**Main expected contribution to photocatalysis**	**Ref.**
Doping	Rare-earth dopants	Nd–ZrO_2	Defect/state engineering; potential visible-light activation; improved charge separation	[82]
Doping	Transition-metal dopants	Mn-ZrO_2, Fe-ZrO_2	Oxygen-vacancy formation and defect levels; reduced e^-/h^+ recombination; enhanced ROS generation	[83, 84]
Doping / metal-assisted	Ag-related (dopant/decoration)	Ag-ZrO_2	Electron trapping / interfacial charge transfer (and possible plasmonic effects, depending on Ag state)	[81, 86]
Doping	Alkaline/other metals	Mg-ZrO_2, Zn-ZrO_2	Tuning of crystallinity/defect chemistry and surface properties (adsorption/hydroxylation), affecting ROS formation	[81, 86]
Loaded / decorated	Noble metals (Schottky junction)	Pd/ZrO_2, Pt/ZrO_2	Metal acts as electron sink (Schottky barrier), suppressing recombination and enhancing apparent kinetics	[88]
Carbon-based hybrids	1D carbon supports	CNT/ ZrO_2	Conductive pathways and higher surface area/adsorption; improved electron transport and reduced recombination	[87]
Carbon-based hybrids	2D carbon supports	rGO-ZrO_2	Fast electron extraction/transport and adsorption enhancement; improved solar/visible response in many cases	[89]
Heterostructure / coupling	Metal/oxide interface (as reported)	Cu/ZrO_2	Interfacial charge transfer and improved light utilization (depending on phase/state and irradiation)	[64]
Organic/inorganic hybrid	Conducting polymer composite	ZrO_2/polyaniline (ternary nanocomposite)	Sensitization/charge-transfer enhancement and adsorption; may improve visible-light response	[39]

Comparative Efficiency and Mechanistic Rationale

To enable a transparent screening of apparent across the selected studies, an approximate pseudo-first-order metric ($k_{app,est}$) was computed from the reported degradation percentages and irradiation times (Table III).

Table III. Comparative screening of apparent efficiencies using an estimated pseudo-first-order rate constant ($k_{app,est}$).

ZrO_2-based system	Light source	Dye	Irradiation time, (min)	Degradation, (%)	$k_{app,est}$ (min^{-1})	Mechanistic rationale
Nd–ZrO_2	VIS	Methylene Blue	20	90	0.115	Rare-earth doping: defect-mediated sub-bandgap excitation and improved charge separation
Nd–ZrO_2	VIS	Rhodamine B	20	77	0.073	Dopant-induced electronic states and suppressed recombination
Mg–ZrO_2	UV	Rhodamine B	60	93	0.044	Oxygen-vacancy/defect engineering; surface chemistry favoring ROS formation
Pd/ ZrO_2	VIS/ UV	Indigo carmine	120	97	0.029	Noble metal as electron sink (Schottky trapping); reduced e^-/h^+ recombination
Ag–ZrO_2	VIS/ UV	Methyl orange	160	99	0.029	Interfacial charge transfer (possible plasmonic contribution depending on Ag state)
Pt/ ZrO_2	Visible/ UV	Indigo carmine	120	95	0.025	Schottky-type electron trapping; sensitive to dispersion/loading
ZrO_2 (pristine)	Visible	RY 160	120	94	0.023	Defects/phase and adsorption contribution under reported conditions
rGO–ZrO_2	Sunlight	Reactive Blue 4	120	93	0.022	Improved electron mobility and interfacial charge transport via conductive carbon
Mn–ZrO_2	Visible	Methyl orange	100	83.7	0.018	Vacancy/defect formation; strong dependence on synthesis/morphology

Note: $k_{app,est}$ was estimated from the reported degradation fraction (D) and irradiation time (t) as $k_{app,est} = -ln(1 - D)/t$. This metric is intended only for transparent, approximate comparison because experimental conditions vary across studies (dye, concentration, pH, light intensity, catalyst loading, etc.).

A direct comparison among ZrO_2-based photocatalysts is often biased by differences in dye chemistry, light source, irradiation intensity, catalyst loading, and pH. Nevertheless, using the reported degradation percentages and irradiation times (Table I), an approximate pseudo-first-order metric ($k_{app,est}$) can be computed to provide a consistent and transparent screening of apparent efficiencies (Table III). Within the compiled studies, rare-earth doping (e.g., Nd– ZrO_2) exhibits the highest apparent rates under visible light, consistent with defect-mediated sub-bandgap excitation and improved charge separation. Transition-metal doping (e.g., Mn–ZrO_2, Mg–ZrO_2) improves performance primarily through oxygen-vacancy engineering and surface chemistry modifications that promote ROS generation. Noble-metal loading (Pd/ ZrO_2, Pt/ ZrO_2) benefits from Schottky-type electron trapping, which suppresses electron–hole (e^-/h^+) recombination. Carbon-based hybrids (e.g., rGO– ZrO_2) demonstrate competitive solar-driven activity due to enhanced electron mobility and interfacial charge transport. Overall, the most efficient architectures share a common feature: they introduce effective charge-separation pathways via defects, junctions, or redox mediators, aligning with reports that oxygen vacancies and engineered electronic states govern ZrO_2 photocatalytic activation under non-UV irradiation.

Adsorption: Due to its high surface area, porous structure, and nanoscale dimensions, ZrO_2 is effective as an adsorbent for organic and inorganic pollutants in water [25]. The adsorption mechanism may involve hydrogen bonding, ligand exchange, or electrostatic interactions [26]. Fig. 7 illustrates how hydrated-ZrO_2 can generate multiple stable active sites, even under acidic conditions. Methods such as sol-gel synthesis [27] and ultrasound-assisted techniques further enhance its efficiency, enabling cost-effective and sustainable applications in industrial wastewater treatment.

Perspectives to Improve Photocatalytic Activity

NP-ZrO_2 has shown significant potential in various applications areas; however, challenges persist in synthesis control, particularly regarding particle size, shape, and aggregation prevention. Crystalline phases unstable at high temperatures limit its durability. At the nanoscale, however, ZrO_2 exhibits unique properties that enable new functional applications. Thin films emerge as a promising alternative, with impact on environmental photocatalysis. In this context, its combination with Anderson–Evans-type polyoxometalates is proposed as a potential approach to optimize photocatalytic efficiency in future applications.

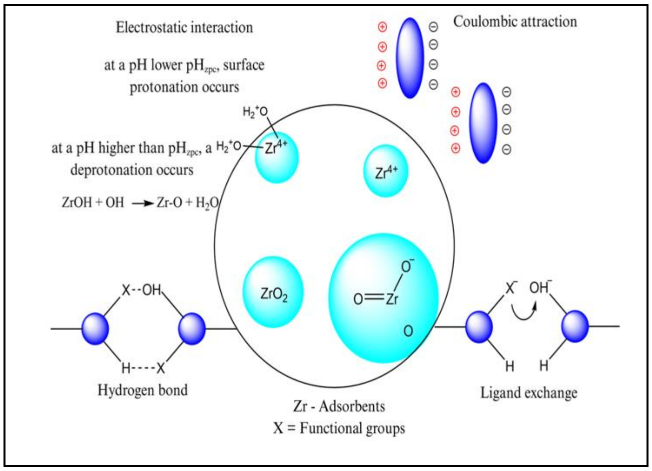

Figure 7. Schematic representation of hydrated ZrO_2 surface interactions, highlighting Zr^{4+} Lewis acidity and adsorption mechanisms via ion exchange and hydrogen bonding.
Source: Adapted from [26]

Thin film deposition: Doctor Blade: Enables ZrO_2 thin films to be deposited in a controlled and economical way, improving their photocatalytic performance. It has been used in sensors and self-cleaning surfaces [28], as shown in Fig. 8.

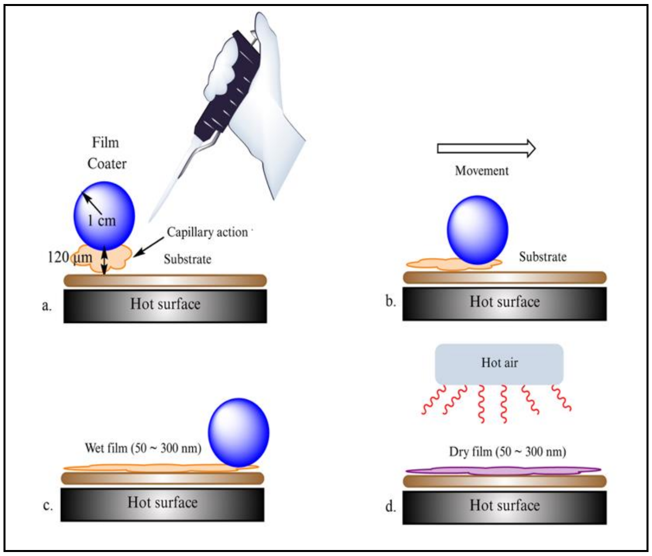

Figure 8. Schematic of the thin film deposition process.
Source: Adapted from [29]

Polyoxometalates (POMs): These are polyanions with redox properties and modifiable structures, useful in catalysis and water treatment applications. They are classified into isopolyanions and heteropolyanions such as Keggin, Anderson–Evans, and Dawson [30].

Anderson-type polyoxometalates (POMs-A): POMs-A have a planar structure and high catalytic capacity. They are modifiable, redox-active, and useful in both homogeneous and heterogeneous catalysis [31]. As shown in Fig. 9, their sub-nano design makes them ideal in advanced treatments and environmental remediation.

ZrO_2-based polyoxometalates: Although POM-As have been more extensively investigated with TiO_2, recent studies [32] report high efficiency when combined with ZrO_2, demonstrating reduced charge recombination and increasing reactive oxygen species. This behavior is illustrated in Fig. 10.

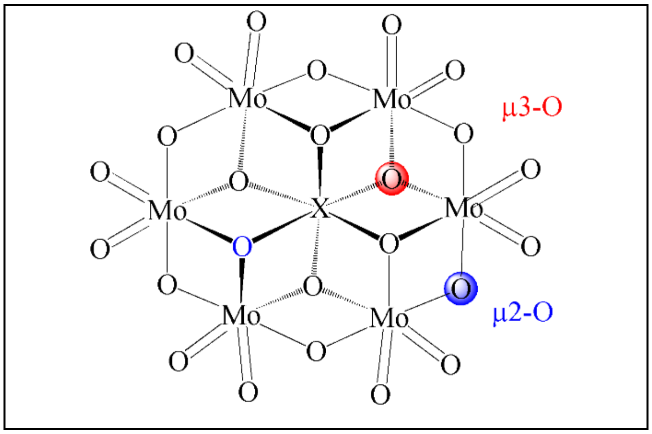

Figure 9. Polyhedral representation of the structure of α-Anderson type POMs.
Source: Authors (created with Chemdraw®)

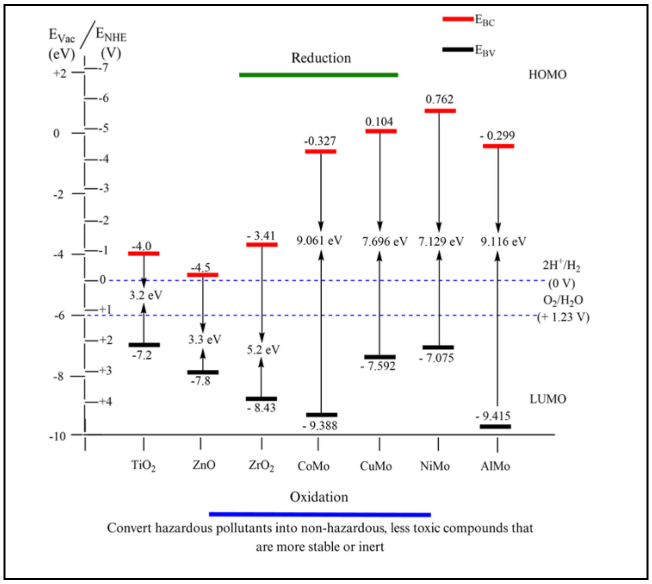

Figure 10. Comparative energy levels of POM-A and metal oxides.
Source: Adapted from [33]

Discussion

The collected results demonstrate the growing interest in ZrO_2 as a photocatalyst, highlighting its structural versatility and redox properties [15], [35]. It is observed that its bandgap limits visible light absorption; strategies such as doping with metals and coupling with other materials, especially Anderson-type polyoxometalates, significantly improve its catalytic efficiency [38], [71]; these modifications reduce e^-/h^+ recombination and extend photocatalytic activity into the visible spectrum [36], [37].

The studies reviewed agree that crystalline phases, controlled synthesis, and the presence of oxygen vacancies are determining factors [14], [43]. However, challenges remain in obtaining stable structures at high temperatures and in the economical scaling of reproducible syntheses. The combination of ZrO_2 with POMs-A appears as a promising yet still underexplored path, especially in thin-film configurations [38], [72].

In addition, the most recent studies have begun to explore the potential of ternary couplings with conductive materials, such as carbon nanotubes or reduced graphene to enhance ZrO_2's electron mobility and long-term photocatalytic stability [13], [49], [63]. Likewise, the interaction with supports such as aerogels also represents an innovative but still underdeveloped alternative [16], [70]. The current challenge lies in transferring these advances to real-world conditions, with complex contaminant matrices and repeated usage cycles. Therefore, a comprehensive approach that combines theoretical modeling, pilot plant testing, and environmental impact analysis is needed for industrial-scale applications.

At a practical level, the findings open possibilities in the treatment of contaminated water and energy devices. Theoretically, they contribute to the design of multifunctional materials with tunable properties. Future research should focus on experimentally validating the stability, selectivity, and efficiency of the hybrid compounds under real conditions.

Perspectives to improve photocatalytic activity

Photocatalytic activity alone is not sufficient for real-world implementation; durability and structural integrity under operating conditions are equally critical. ZrO_2 is widely recognized for its high chemical resistance and stability over a broad temperature range, which makes it attractive as a robust oxide platform for photocatalysis [73]. However, in practical aqueous systems—especially under extreme pH or in the presence of aggressive ions—zirconia-based materials may still undergo degradation processes that ultimately reduce performance. For stabilized zirconia ceramics, corrosion-like behavior can involve preferential dissolution of stabilizing species and measurable ion release in strongly acidic or basic media, potentially inducing phase transformations that affect long-term functionality [74]. In thin-film configurations, chemical durability can depend on deposition route and post-treatments. ZrO_2 films can exhibit measurable etch rates in acidic environments, indicating that "corrosion" for ZrO_2-based layers should be discussed as dissolution/etching and/or film delamination rather than metallic corrosion in the classical sense [75].

For doped and heterostructured ZrO_2, stability is strongly governed by the least stable component. Several deactivation mechanisms should be considered in the context of dye degradation: (i) dopant leaching (transition metals, rare-earths, or noble metals) and subsequent loss of catalytic sites; (ii) surface fouling by strongly adsorbed intermediates/by-products, which blocks active sites; (iii) particle aggregation/sintering (more relevant in powders) that reduces surface area; (iv) phase evolution (*e.g.*, tetragonal to monoclinic fraction changes depending on synthesis/thermal history); and (v) photodegradation or photocorrosion of the coupled partner in heterostructures (notably for some visible-active semiconductors), which can dominate durability even if ZrO_2 itself remains stable.

In ZrO_2–POM hybrids, an additional issue is the intrinsic leaching/solubility risk of polyoxometalates in aqueous media. Recent reviews highlight that POM-based photocatalytic materials can suffer from leaching and stability limitations, which is precisely why heterogenization/immobilization strategies are often emphasized to enable long-term operation [76]. Consistent with this, POM functionalization and immobilization on solid supports (metal oxides, carbon materials, polymers, MOFs, etc.) are commonly proposed as routes to reduce POM loss while preserving the redox/charge-transfer benefits that POMs bring to photocatalytic processes [77]. Therefore, the thin-film approach (immobilizing POMs on ZrO_2 films) is not only relevant for charge-transfer enhancement but also potentially advantageous for operational stability compared with purely dispersed molecular POM systems. However, adhesion strength and leaching resistance must be experimentally validated.

To strengthen future ZrO_2 photocatalysis studies and support scale-up claims, stability should be evaluated and reported using a minimal set of tests: (a) cycling/reusability (at least 5 cycles) with quantitative activity retention; (b) post-reaction characterization (XRD/SEM and, when possible, XPS) to verify structural and surface chemical integrity; and (c) leaching assays using elemental analysis (ICP-OES/ICP-MS) to quantify dissolution of dopants, coupled partners, or POM components. The use of ICP-based leaching confirmation is increasingly standard in photocatalysis durability reporting [78]. In film-based catalysts, additional reporting of film adhesion/delamination behavior after cycling is recommended, as apparent stability in activity may mask gradual detachment or surface damage.

Conclusions

The review consolidates current knowledge on the synthesis, modification, and application of ZrO_2 in heterogeneous photocatalysis processes, especially for the degradation of organic contaminants in aqueous solutions. ZrO_2 exhibits favorable physicochemical properties—including thermal stability, high density of oxygen vacancies, and the possibility of adjusting its crystalline structure—positioning it as a promising material for environmental remediation.

The potential of ZrO_2 thin films as a support for Anderson-type polyoxometalates is highlighted as an innovative strategy with promising theoretical results but still lacking experimental validation. The combination could improve quantum efficiency and extend the spectral response of ZrO_2 toward the visible region.

Among the main limitations is the difficulty in maintaining phase stability at high temperatures and the need for more reproducible, sustainable, and low-cost synthesis processes.

It is recommended that future research explore the practical application of ZrO_2/POMs-A hybrid compounds, including studies on service life, recyclability, and performance under real operating conditions. Furthermore, their performance in solar reactors or integrated systems for pilot-scale water treatment warrants systematic evaluation.

Author contributions

Jiress Florez: Conceptualization, methodology, investigation, data curation, formal analysis, visualization, writing of the original draft, and review and editing.
Carlos Díaz-Uribe: Conceptualization, methodology, supervision; validation, writing, review, and editing.
William Vallejo: methodology, investigation, data curation, validation, writing, review, and editing.
All authors: Read and approved the final version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

The data that support the findings of this study are not publicly available due to the nature of the research and are not hosted on any repository.

Statement on artificial intelligence

The authors did not use IAG. The authors take full responsibility for the contents of this publication

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