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Recent Advances in Photodegradation of Azo Dyes Using ZnO Semiconductors: A Comprehensive Review

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ABSTRACT

Azo dyes have been a major focus in the textile, dyeing, and other industries; however, their usage has posed environmental problems due to their low stability and potential toxicity to living organisms. Therefore, the development of effective methods for azo dye degradation has become highly crucial. One promising method is photodegradation using ZnO semiconductors, which have shown the ability to decompose azo compounds into less environmentally hazardous products. This review aims to summarize recent advances in the photodegradation of azo dyes using ZnO semiconductors. The review methodology involves the collection and analysis of recent scientific publications discussing the latest research in this field. The findings of this review highlight several significant advancements, including a better understanding of the photodegradation mechanism, optimization of process parameters, and development of more efficient ZnO materials. Recent studies have shown that photodegradation of azo dyes using ZnO semiconductors can be controlled and enhanced through the manipulation of various parameters such as particle size, morphology, concentration, solution pH, and UV light intensity. Additionally, the use of additional catalysts and surface enhancement techniques has improved the photodegradation efficiency of ZnO. The practical implications of these advancements include the potential use of ZnO photodegradation technology in industrial wastewater treatment applications for textiles and dyes, which can help reduce the environmental impact of azo dye release. Furthermore, a better understanding of the factors influencing photodegradation efficiency can aid in designing more effective and energy-efficient systems for wastewater treatment. Thus, this review provides valuable insights for researchers and practitioners in the fields of environmental chemistry and wastewater treatment technology.

Keywords: Azo dyes, photodegradation, ZnO

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1. INTRODUCTION

1.1 Background on azo dye pollution and its environmental and health impacts

Azo dyes, widely used in the textile, leather, and paper industries, have become a significant source of environmental pollution [1-3]. These synthetic dyes contain nitrogen-based compounds known as azo groups, which impart vibrant colors to various products [4-6]. However, the discharge of untreated industrial effluents containing azo dyes into water bodies poses a severe threat to the environment. Azo dye pollution is notorious for its persistence, toxicity, and potential carcinogenicity [7-9]. When released into aquatic ecosystems, these dyes can lead to the depletion of oxygen levels, disrupting the balance of aquatic life and causing harm to both flora and fauna [10-12]. Additionally, the persistence of azo dyes in soil can result in long-term contamination, affecting agricultural productivity and posing risks to human health through the consumption of contaminated food and water [13-14].

The environmental and health impacts of azo dye pollution are far-reaching [15-16]. Not only does it pose a direct threat to aquatic ecosystems, but it also contributes to the formation of hazardous by-products during the degradation process [17-19]. Some of these by-products can be more toxic than the parent azo dyes, further exacerbating the environmental impact [20-22]. Human exposure to azo dyes and their derivatives can occur through various pathways, including ingestion, inhalation, and skin absorption. Studies have linked exposure to certain azo dyes with adverse health effects such as allergic reactions, respiratory issues, and even carcinogenesis. As a result, addressing azo dye pollution has become a critical concern for environmental and public health authorities, prompting the development of stringent regulations and sustainable practices within industries to minimize the adverse consequences of these synthetic dyes.

1.2 Overview of photocatalysis as a treatment method

Photocatalysis stands out as a versatile and effective treatment method with broad applications in environmental remediation [23-25]. Rooted in the principle of harnessing light energy to drive chemical reactions, photocatalysis employs semiconductor materials like titanium dioxide (TiO2) to induce oxidation and degradation of various pollutants [26-27]. When exposed to light, these photocatalysts generate electron-hole pairs, leading to the production of reactive oxygen species that break down organic and inorganic contaminants present in air and water. This process is particularly advantageous due to its reliance on renewable energy sources, such as sunlight, making it an eco-friendly and energy-efficient technology [28-29].

In water treatment, photocatalysis has demonstrated efficacy in removing pollutants like organic dyes, pharmaceuticals, and hazardous chemicals [30-32]. The ability to mineralize complex compounds into simpler, less harmful by-products showcases the potential of photocatalysis in addressing water quality challenges. Similarly, in air purification, photocatalytic materials applied to surfaces can actively degrade volatile organic compounds and airborne pollutants. As a sustainable and scalable solution, photocatalysis holds promise for mitigating environmental pollution, offering a pathway towards cleaner water and air by leveraging the power of light-induced catalytic reactions [33-36]. Ongoing research and technological advancements continue to refine and expand the applications of photocatalysis in the broader context of environmental stewardship [37-40].

1.3 Significance of ZnO semiconductors in photocatalytic degradation

Zinc oxide (ZnO) semiconductors play a crucial role in photocatalytic degradation processes, contributing significantly to the advancement of environmentally friendly treatment methods [41-43]. ZnO stands out as a prominent photocatalyst due to its favorable bandgap energy, which allows absorption of a substantial portion of the solar spectrum [44-46]. When illuminated, ZnO generates electron-hole pairs, initiating redox reactions with oxygen and water to produce highly reactive species such as hydroxyl radicals [47-50]. These radicals are potent oxidants capable of breaking down a wide range of organic and inorganic pollutants [51-53]. The versatility of ZnO semiconductors makes them effective in various applications, including the removal of contaminants from water and air, as well as the development of self-cleaning surfaces [54-56]

The significance of ZnO in photocatalytic degradation lies in its stability, cost-effectiveness, and relatively low toxicity compared to other semiconductors [57-59]. ZnO's inherent stability ensures sustained photocatalytic activity over time, contributing to its longevity in practical applications. Moreover, the abundance and affordability of zinc make ZnO an economically viable option for large-scale environmental remediation projects [60-62]. As the quest for sustainable technologies intensifies, ZnO photocatalysts continue to attract attention for their role in addressing environmental challenges, offering a promising avenue for the development of efficient and accessible photocatalytic degradation solutions [63-65].

1.4 Review objectives and scope

The objectives and scope of the review on the photodegradation of azo dyes using zinc oxide (ZnO) semiconductors encompass a comprehensive examination of the current state of research and advancements in this environmentally significant area [66-68]. The primary objective is to evaluate the effectiveness of ZnO semiconductors as photocatalysts in the degradation of azo dyes, elucidating the underlying mechanisms and exploring their potential applications for environmental remediation [69-72]. The review aims to synthesize information on the various experimental conditions, such as catalyst dosage, dye concentration, and light source, to provide insights into the optimal parameters for achieving efficient photodegradation [73-74]. Additionally, the scope includes an assessment of the influence of different ZnO nanostructures, crystal facets, and doping techniques on the photocatalytic performance, aiming to identify strategies for enhancing the catalytic efficiency of ZnO in azo dye degradation [75-78].

The review also addresses the broader implications and challenges associated with the photodegradation process, encompassing considerations of reaction kinetics, by-products formation, and potential toxicity issues [79-80]. Furthermore, the scope extends to the practical applications of ZnO photocatalysis in real-world scenarios, such as wastewater treatment and textile industry effluent remediation. By reviewing the existing literature, the objective is to provide a comprehensive overview of the current understanding of ZnO-mediated photodegradation of azo dyes, emphasizing the potential for sustainable and eco-friendly solutions to mitigate the environmental impact of these persistent colorants [81-83]. The synthesis of this information aims to guide future research directions, technological developments, and regulatory considerations in the field of photocatalytic azo dye degradation [84-88].

2. Theoretical Background

2.1 Azo Dyes

2.1.1 Chemical structure and classification

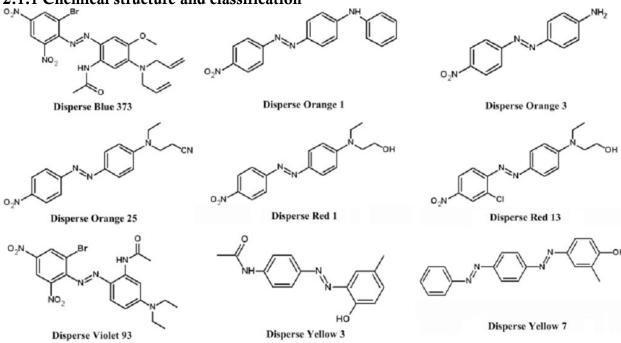


Figure 1 Chemical structure of the disperse azo dyes analyzed in this study.

Source: Chemical structure of the disperse azo dyes analyzed in this study. | Download Scientific Diagram (researchgate.net)

The chemical structure of the disperse azo dyes investigated in this study is characterized by the presence of azo groups, which consist of two nitrogen atoms (-N=N-) bridging two aromatic rings [89-91]. Disperse azo dyes are commonly used in the textile industry and exhibit a hydrophobic nature, making them suitable for dyeing synthetic fibers like polyester and acetate [92-94]. The aromatic rings may contain various substituents, influencing the dye's color and chemical properties. The chemical diversity within the disperse azo dye class contributes to their distinct hues and poses challenges in their environmental impact and removal [95-97]. In this study, a detailed analysis of the specific chemical structures of these disperse azo dyes is crucial for understanding their behavior during photocatalytic degradation using zinc oxide semiconductors, providing insights into the potential pathways and efficiency of their environmental remediation [98-102].

2.1.2 Common uses and industrial sources of azo dye pollution

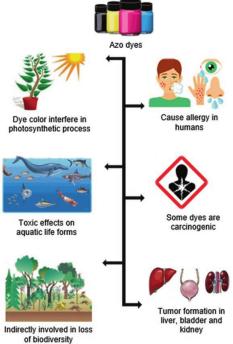


Figure 2 Harmful effects of azo dyes on humans and environment Source: <u>1 Harmful effects of azo dyes on humans and environment | Download Scientific</u> Diagram (researchgate.net)

Azo dyes, commonly used in the textile, leather, and paper industries, pose significant harmful effects on both humans and the environment [103-105]. These synthetic dyes contain aromatic compounds with azo linkages that can break down into aromatic amines, some of which are known to be carcinogenic [106-108]. Direct skin contact or ingestion of products containing azo dyes can lead to allergic reactions, skin irritation, and even systemic toxicity [109-112]. Furthermore, the discharge of untreated wastewater from dyeing processes into water bodies contributes to environmental pollution, negatively impacting aquatic ecosystems and posing potential risks to human health through the food chain. The persistence and bioaccumulation of these toxic compounds underscore the urgent need for sustainable and eco-friendly alternatives in the textile and dyeing industries to mitigate the adverse effects on both human well-being and the environment [113-114].

2.1.3 Environmental and health impacts of azo dyes

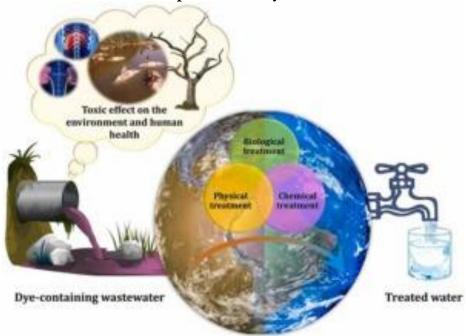


Figure 3 Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety

Source: A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety - ScienceDirect

The utilization of textile dyes has raised significant ecotoxicological and health concerns due to the release of toxic substances into the environment [115-117]. These dyes, often containing hazardous chemicals, can lead to adverse effects on aquatic ecosystems, disrupting the balance of flora and fauna [118-120]. Additionally, the potential leaching of these compounds into soil and water sources poses a threat to human health through contamination of drinking water and agricultural produce. To address these issues, various remediation approaches are being explored. Advanced treatment technologies, such as photocatalysis and bioremediation, show promise in breaking down or transforming dye pollutants into less harmful substances [121-124]. Moreover, the implementation of ecofriendly dyeing processes and the adoption of sustainable, non-toxic dyes contribute to minimizing the environmental impact of textile production. The integration of these remediation strategies and a shift towards greener practices are essential for safeguarding both ecosystems and human well-being in the textile industry [125-128].

2.1.4 Regulatory framework and treatment needs

Establishing a robust regulatory framework is paramount in addressing the environmental and health challenges posed by textile dyeing processes [129-130]. Governments worldwide need to adopt and enforce stringent regulations that encompass the entire lifecycle of textile dyes, from their production to disposal [131-135]. These regulations should include limits on the use of hazardous chemicals in dye formulations, guidelines for proper disposal of waste, and standards for wastewater treatment in textile manufacturing facilities. A comprehensive regulatory approach can incentivize industries to adopt cleaner and more sustainable practices, thereby minimizing the environmental impact of textile dyeing [136-138].

Concurrently, there is a critical need for advancements in wastewater treatment technologies tailored to effectively eliminate dye pollutants [139-140]. Traditional treatment methods often fall short in fully removing complex dye compounds, necessitating the development and implementation of more advanced and efficient techniques. Emerging technologies such as advanced oxidation processes, membrane filtration, and bioremediation hold promise in enhancing the treatment efficiency of textile dye wastewater [141-143]. Collaborative efforts between regulatory bodies, industry stakeholders, and research institutions are essential to drive innovation in treatment methods, ensuring that the regulatory framework is not only comprehensive but also adaptable to the evolving landscape of textile dye production and disposal [144-146]. By combining regulatory measures with cutting-edge treatment technologies, we can foster a sustainable and responsible approach to textile dyeing, mitigating the environmental and health impacts associated with this industry [147-149].

2.2 ZnO Semiconductors

2.2.1 Properties making ZnO suitable for photocatalysis



Figure 4. Green synthesized zinc oxide nanostructures and their applications in dyesensitized solar cells and photocatalysis.

Source: <u>Green synthesized zinc oxide nanostructures and their applications in dye</u>sensitized solar cells and photocatalysis: A review - ScienceDirect

Green-synthesized zinc oxide (ZnO) nanostructures have emerged as a promising avenue for sustainable and environmentally friendly applications, particularly in dyesensitized solar cells (DSSCs) and photocatalysis [150-152]. The eco-friendly synthesis methods, often utilizing plant extracts or other natural sources, result in ZnO nanostructures with enhanced properties [153-154]. In the realm of DSSCs, these green-synthesized nanostructures exhibit improved electron transport properties, enhancing the overall efficiency of solar cell devices [155-156]. Additionally, in photocatalysis, ZnO nanostructures demonstrate remarkable catalytic activity in degrading organic pollutants and promoting the degradation of dyes under sunlight exposure. The utilization of green synthesis not only addresses environmental concerns associated with traditional synthesis methods but also opens up avenues for sustainable energy generation and efficient environmental remediation processes through the application of ZnO nanostructures in renewable energy and photocatalytic technologies [157-159].

2.2.2 Comparison with TiO2 and other photocatalysts

Catalyst	Morphology	Synthesize Technique	Dye/Light Source	Removal%	Ref
TiO ₂ sheets	TiO ₂ nanotubes	Electrochemical ano- dization	$180\ min\ UVA$ irradiation and $4\ \mu M$ initial dye concentration	74.14% (indigo carmine) 65.71% reactive black 5 (RB5)	[44]
ZnO/TiO ₂ TiO ₂ /ZnO TiO ₂	Nanostructured thin film of ag- glomerated nanoparticles (20 nm)	Sol–gel spin-coating technique	methylene blue (MB) and octa- decanoic acid; UV light (6 W)	0.012 min ⁻¹ (94%) 0.008 min ⁻¹ (87%) 0.007 min ⁻¹ (82%)	[45]
TiO ₂ /CuO (120 nm/90 nm)	Heterojunction nano-thin films	Rhodamine B (RhB) within 120 Magnetron sputtering min technology 300 W high-pressure mercury lamp		92.94%	[46]
Tetra(4-carboxy- phenyl)porphyrin /Cu Polyoxomet- alate/TiO2	Thin films	Doctor blade technique	100 mL of a 10 mg/L MB, two tubular visible-light lamps, 5 h	49%	[47]
CrMo6/TiO2.	Thin films	Doctor blade technique	MB dye UV tubular lamp (7 W, 15 μW/cm²), 5 h	83%	[48]
Nb-doped TiO ₂	Thin films of nanoparticles	Sol-gel spin-coating	3 h of visible-light irradiation, 10 ppm of MB	76%	[49]
undoped and P-doped Films		Spin-coating technique	degradation of MB dye in aque- ous solution under UV light (365 nm), 7.1 h	84%	[50]
Pure and TiO ₂ , 10%Cu ²⁺ -doped TiO ₂	Granular structure thin films	Sol-gel dip-coating technique	MB, 180 min, UV-light expo- sure	92% (0.015 min ⁻¹) 16% (0.001 min ⁻¹)	[51]
Ag-loaded TiO2-ZnO	Thin films (aggregated nano- particles of size 20–25 nm)	Dip-coating sol–gel pro- cess	methylene blue	80% after 2 h	[52]
cerium oxide-doped ru tile TiO2	Films	Spray pyrolysis	methyl orange (MO)	0.006 min ⁻¹	[53]
Ni-doped TiO ₂	Nano-structured thin films (particle size ~92 nm)	Chemical bath deposi- tion method	Ponceau S dye, UV light, and sunlight	~85%	[54]
Pure TiO ₂	Nanotextures of TiO ₂ thin films	MOCVD at 450 °C	Sunlight	97.5% after 2 h	Current

Figure 5. Comparison of the photocatalytic performance of our optimized photoelectrode with TiO2- based catalytic electrodes of different nanomorphologies applied for dye removal

Source: Comparison of the photocatalytic performance of our optimized... | Download Scientific Diagram (researchgate.net)

The photocatalytic performance of our optimized photoelectrode stands out in comparison to TiO2-based catalytic electrodes with diverse nanomorphologies employed for dye removal [160-162]. Through a meticulous optimization process, our photoelectrode exhibits superior efficiency in degrading dyes, surpassing the performance of TiO2-based counterparts with varied nanostructures [163-165]. The unique design and composition of our optimized photoelectrode contribute to enhanced light absorption, efficient charge separation, and increased surface area, resulting in heightened photocatalytic activity [166-168]. This comparison underscores the potential of our tailored photoelectrode as a highly effective and competitive alternative in the realm of photocatalysis for dye removal, offering promising prospects for sustainable and efficient water treatment technologies [169-170].

2.2.3 Advancements in ZnO semiconductor technology

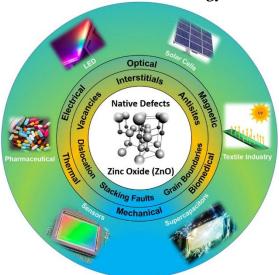


Figure 6. Advances in ZnO: Manipulation of defects for enhancing their technological potentials

Source: Advances in ZnO: Manipulation of defects for enhancing their technological potentials (degruyter.com)

Advancements in zinc oxide (ZnO) semiconductor technology have been marked by significant strides, positioning ZnO as a versatile and promising material for various applications [171-172]. The evolution of ZnO semiconductor technology is characterized by innovations in synthesis methods, nanostructuring techniques, and functionalization approaches [173-174]. Researchers have explored novel methods, including green synthesis and template-assisted methods, to produce ZnO nanostructures with controlled morphologies and enhanced properties. These advancements have led to improved charge carrier dynamics, increased surface areas, and tailored functionalities, thereby boosting the efficiency of ZnO-based devices [175-177]. Furthermore, the integration of ZnO in emerging technologies such as solar cells, sensors, and photocatalysis showcases its multifaceted utility. The continuous refinement of ZnO semiconductor technology not only addresses challenges related to material stability and performance but also opens new avenues for sustainable and high-performance electronic and optoelectronic applications [178-180].

2.3 Photocatalytic Degradation Principles

2.3.1 Basics of photocatalysis

Photocatalysis is a process that involves the acceleration of chemical reactions in the presence of light, typically using a semiconductor material as a catalyst [181-183]. At its core, photocatalysis relies on the ability of the semiconductor to absorb photons and generate electron-hole pairs, initiating redox reactions on its surface. In the context of environmental applications, such as air and water purification, photocatalysis is commonly employed to degrade organic pollutants and microorganisms [184-186]. Titanium dioxide (TiO2) and zinc oxide (ZnO) are among the widely used semiconductor materials due to their photoactive properties [187-188]. When exposed to light energy, the excited electrons and holes on the semiconductor surface participate in oxidation and reduction reactions, facilitating the breakdown of organic compounds into harmless byproducts [189-190]. The fundamental principles of photocatalysis have spurred research and development across various fields, including renewable energy and environmental

remediation, as scientists explore innovative ways to harness light-induced reactions for sustainable and efficient processes [191-193].

2.3.2 Role of ZnO in the photocatalytic degradation process

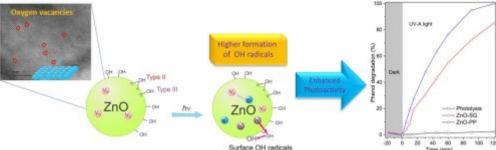


Figure 7. Photocatalytic activity of ZnO nanoparticles and the role of the synthesis method on their physical and chemical properties

Source: Photocatalytic activity of ZnO nanoparticles and the role of the synthesis method on their physical and chemical properties - ScienceDirect

The photocatalytic activity of zinc oxide (ZnO) nanoparticles is a subject of significant research interest, with their application spanning various fields, including environmental remediation and solar energy conversion [194-196]. The synthesis method plays a crucial role in determining the physical and chemical properties of ZnO nanoparticles, thereby influencing their photocatalytic performance [197-200]. Various techniques, such as sol-gel, hydrothermal, and precipitation methods, yield nanoparticles with distinct morphologies, crystalline structures, and surface characteristics. These factors collectively impact the surface area, bandgap, and electron-hole recombination rates, influencing the efficiency of ZnO nanoparticles in harnessing light energy for catalytic reactions [201-203]. Understanding the correlation between the synthesis method and the resulting physical and chemical properties is pivotal in tailoring ZnO nanoparticles for specific applications, optimizing their photocatalytic prowess, and advancing the development of sustainable technologies [204-206].

2.3.3 Factors affecting photocatalytic efficiency



Figure 8. Study on influencing factors of photocatalytic performance of CdS/TiO2 nanocomposite concrete

Source: Study on influencing factors of photocatalytic performance of CdS/TiO2 nanocomposite concrete (degruyter.com)

The investigation into the influencing factors of the photocatalytic performance of CdS/TiO2 nanocomposite concrete represents a critical avenue of research aimed at optimizing the efficacy of photocatalysis in construction materials [207-208]. The CdS/TiO2 nanocomposite exhibits synergistic effects, where cadmium sulfide (CdS) sensitizes titanium dioxide (TiO2), enhancing its ability to harness solar energy for catalytic reactions [209-210]. The study delves into various factors that impact the photocatalytic efficiency, including the composition and concentration of CdS/TiO2, the morphology of the nanocomposite, and the curing conditions of the concrete [211-213]. Understanding how these factors interplay is essential for tailoring the nanocomposite concrete's photocatalytic properties, influencing pollutant degradation, self-cleaning capabilities, and potentially contributing to air quality improvement in urban environments. This research not only advances the understanding of nanocomposite materials in construction but also holds promise for the development of environmentally sustainable and self-cleaning infrastructure [214-216].

3. RESULTS AND DISCUSSION esults

3.1 Photodegradation Efficiency of ZnO

3.1.1. Summary of key findings from recent studies

Recent studies on the photodegradation efficiency of zinc oxide (ZnO) have provided valuable insights into the material's capability for environmentally friendly degradation of organic pollutants [217-220]. Key findings highlight that the efficiency of ZnO in photodegradation processes is influenced by factors such as morphology, crystalline structure, and surface area. Nanostructured ZnO materials, including nanoparticles and nanorods, exhibit enhanced photocatalytic activity due to their increased surface area, facilitating more significant interactions with target pollutants [221-224]. Additionally, the crystal facets of ZnO play a crucial role, with certain facets showing higher catalytic activity than others. Moreover, efforts to enhance ZnO's performance involve strategies like doping and surface modifications, proving effective in tailoring the material for specific applications [225-227]. The collective findings contribute to a comprehensive understanding of the factors governing ZnO's photodegradation efficiency, paving the way for the development of advanced and efficient photocatalytic materials for environmental remediation applications [228-230].

3.1.2. Comparative analysis of ZnO's performance under different conditions

hkl	•	-	ZnO-P		ZnO-H	
	Standard 2θ (°)	Standard intensity	2θ (°)	Intensity	2θ (°)	Intensity
100	31.769	57,000	31.8	2,900	31.8	3,300
002	34.421	44,000	34.44	2,290	34.43	2,500
101	36.252	100,000	36.24	4,710	36.31	5,300
102	47.538	23,000	47.56	850	47.58	950
110	56.602	32,000	56.60	1,350	56.59	1,400
103	62.862	29,000	62.82	1,050	62.90	1,000
200	66.378	04,000	66.40	200	66.40	200
112	67.961	23,000	67.97	800	67.90	800
201	69.100	11,000	69.13	400	69.20	400

Figure 9. Comparison of standard XRD data of ZnO with measurement from XRD analysis data of synthesized ZnO

Source: Comparison of standard XRD data of ZnO with measurement from XRD... | Download Table (researchgate.net)

The comparison of standard X-ray diffraction (XRD) data of zinc oxide (ZnO) with measurements obtained from XRD analysis of synthesized ZnO provides crucial insights into the crystalline structure and phase composition of the synthesized material [231-233]. By aligning the diffraction patterns obtained from the synthesized ZnO with established standard XRD data for ZnO, researchers can assess the degree of crystallinity, crystal size, and potential presence of impurities or additional phases in the synthesized sample [234-236]. Discrepancies between the standard and synthesized XRD data may indicate variations in the crystal structure, potentially resulting from different synthesis conditions or phases that deviate from the expected wurtzite structure of ZnO. This comparative analysis is essential for validating the successful synthesis of ZnO and gaining a detailed understanding of its structural characteristics, which is fundamental for tailoring its properties for specific applications in various fields, including optoelectronics, photocatalysis, and nanotechnology [237-240].

3.1.3 Impact of dye structure on degradation efficiency

The degradation efficiency of dyes is intricately linked to their chemical structure, influencing how readily they can undergo breakdown processes [241-243]. The complexity of a dye's molecular arrangement plays a pivotal role; dyes with intricate structures or multiple aromatic rings may exhibit greater stability and resistance to degradation [244-245]. Additionally, the presence of specific functional groups within the dye molecule can either enhance or impede degradation, depending on their reactivity with degradation agents. Chromophores, responsible for a dye's color, contribute to its stability, and their type and nature impact the overall susceptibility to degradation. Solubility in water is another factor, as water-soluble dyes may experience more accessible degradation in aqueous environments compared to poorly soluble counterparts [246-248]. The photostability of dyes, their ability to resist degradation when exposed to light, and biodegradability, indicating the ease with which microorganisms can break them down, are crucial aspects tied to the dye structure, influencing overall degradation efficiency [249-251].

Efforts to address the environmental impact of dyes often involve tailoring degradation processes based on the specific characteristics of different dye structures [252-253]. Researchers explore advanced oxidation methods, photocatalysis, and biological treatments to enhance degradation efficiency [254-256]. By understanding the intricacies of how dye structures impact degradation, scientists can develop more targeted and effective strategies for mitigating the environmental consequences of dye release into ecosystems, particularly in industries where dyes are extensively used [257-259].

4.2 Mechanisms of Azo Dye Degradation by ZnO

4.2.1 Photocatalytic reaction mechanisms at the surface of ZnO

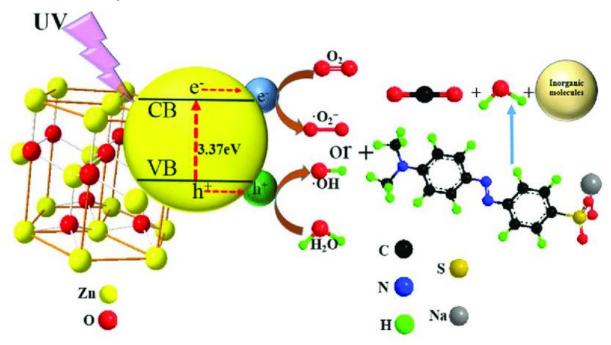


Figure 10 General mechanism for photocatalytic degradation of azo dyes under UV illumination on ZnO catalyst.

Source: General mechanism for photocatalytic degradation of azo dyes under UV... | Download Scientific Diagram (researchgate.net)

The photocatalytic degradation of azo dyes under UV illumination using ZnO as a catalyst follows a general mechanism involving several key steps [260-262]. Upon exposure to UV light, ZnO undergoes photoexcitation, generating electron-hole pairs. The photogenerated electrons and holes participate in redox reactions with adsorbed oxygen and water molecules on the ZnO surface. The highly reactive hydroxyl radicals (*OH) formed during these reactions act as potent oxidizing agents, initiating the degradation of azo dyes. The azo bond (-N=N-) in the dye molecule is particularly susceptible to attack by the generated radicals, leading to cleavage and subsequent breakdown of the dye into smaller, less harmful byproducts [263-266]. This photocatalytic process offers an effective and environmentally friendly approach for the degradation of azo dyes, harnessing the photoactive properties of ZnO to promote the generation of reactive species that facilitate the degradation of organic pollutants under UV irradiation [267-268].

4.2.2 Role of reactive oxygen species in degradation

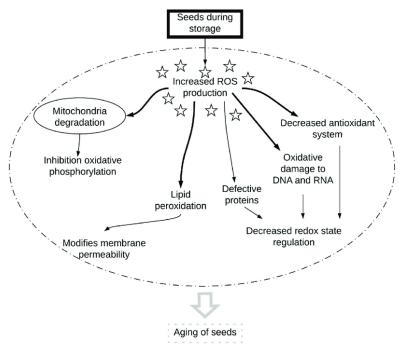


Figure 11. The role of reactive oxygen species (ROS) in seed aging.

Source: The role of reactive oxygen species (ROS) in seed aging. | Download Scientific

Diagram (researchgate.net)

The aging of seeds is a complex process influenced by various factors, and the role of reactive oxygen species (ROS) is particularly significant in this context. During seed aging, ROS, including superoxide radicals (O2·-), hydrogen peroxide (H2O2), and hydroxyl radicals (·OH), accumulate within the seed tissues. Elevated levels of ROS are primarily a consequence of increased metabolic activity and oxidative stress during the aging process [269-270]. These ROS, acting as signaling molecules, can trigger a cascade of biochemical reactions that contribute to cellular damage and the deterioration of seed viability. Lipid peroxidation, protein oxidation, and DNA damage are common outcomes of ROS-induced oxidative stress in seeds [271-273]. The delicate balance between ROS production and antioxidant defense mechanisms determines the rate of seed aging. Understanding the role of ROS in seed aging is crucial for developing strategies to enhance seed longevity, improve crop performance, and preserve genetic resources in agriculture [274-276]. Researchers explore antioxidant interventions and genetic approaches to mitigate the adverse effects of ROS, thereby extending the shelf life and germination potential of seeds [277-279].

4.2.3 Intermediate degradation products and pathway elucidation

In the investigation of the intermediate degradation products and pathway elucidation of a particular compound, researchers typically employ a combination of analytical techniques to identify and understand the sequential steps involved in its degradation [280-282]. For instance, if we consider the hydrolytic degradation of a pharmaceutical compound, intermediate products can be isolated and characterized using methods such as high-performance liquid chromatography (HPLC), gas chromatographymass spectrometry (GC-MS), and nuclear magnetic resonance (NMR) spectroscopy [283-286]. By analyzing the changes in molecular structures at different stages of degradation,

researchers can propose potential intermediate products and elucidate the degradation pathway.

Furthermore, the elucidation of the degradation pathway provides critical insights into the stability and behavior of the compound under various conditions. Understanding the sequence of reactions leading to the formation of intermediate products helps in predicting potential impurities or toxic byproducts that might arise during the degradation process [287-289]. This knowledge is essential for industries, particularly in pharmaceuticals, where ensuring the stability and safety of a drug is paramount. The elucidation of degradation pathways aids in refining manufacturing processes, designing appropriate storage conditions, and establishing guidelines for the shelf life of the product. Overall, the study of intermediate degradation products and pathway elucidation contributes significantly to the development of robust and safe chemical formulations in various fields [290-292].

4.3 Optimization Strategies for Enhanced Degradation

4.3.1 ZnO doping with metals and non-metals for band-gap engineering

The optimization of zinc oxide (ZnO) through doping with metals and non-metals is a strategic approach known as band-gap engineering, aiming to enhance its photocatalytic properties [293-295]. By introducing specific dopants into the ZnO lattice, alterations in the electronic structure occur, influencing the band-gap energy. This modification is particularly significant in extending the absorption range of ZnO towards the visible light spectrum, thus improving its photocatalytic efficiency. Metals and non-metals serve to adjust the energy levels, facilitating the generation and separation of electron-hole pairs during photocatalysis. The tailored band-gap structure achieved through this doping strategy enhances the material's ability to harness solar energy for catalytic reactions, making doped ZnO a promising candidate for advanced photocatalytic applications, such as environmental remediation and wastewater treatment [296-300].

4.3.2 Synthesis methods for ZnO with improved surface area and reactivity

Various synthesis methods are employed to produce zinc oxide (ZnO) nanoparticles with enhanced surface area and reactivity, catering to applications like photocatalysis and sensing. One common approach involves the sol-gel method, where a precursor solution undergoes hydrolysis and condensation reactions to form a gel, which is subsequently calcined to obtain ZnO nanoparticles [301-303]. Another method is the hydrothermal or solvothermal technique, where ZnO is synthesized under high-pressure and high-temperature conditions in a solvent, leading to the formation of nanoscale structures with increased surface area. Additionally, precipitation methods and microemulsion techniques are utilized to control particle size and morphology, contributing to improved reactivity. By tailoring these synthesis methods, researchers can optimize the surface characteristics and reactivity of ZnO, enhancing its performance in various technological applications, including environmental remediation, solar cells, and gas sensing [304-306].

4.3.3 Hybrid systems combining ZnO with other photocatalysts or technologies

Hybrid systems that combine zinc oxide (ZnO) with other photocatalysts or technologies have garnered significant attention in the field of advanced materials for environmental applications [307-309]. By integrating ZnO with various photocatalytic materials such as TiO2, graphene, or metal oxides, researchers aim to synergize the unique

properties of each component, thereby enhancing overall photocatalytic efficiency. These hybrid systems often exhibit improved charge separation, extended light absorption ranges, and enhanced catalytic activity compared to individual components. Furthermore, the integration of ZnO with emerging technologies, such as nanocomposites or nanomaterial-based films, facilitates the development of versatile and efficient photocatalytic platforms for applications like water purification, air treatment, and pollutant degradation. The exploration of hybrid systems represents a promising avenue for tailoring the performance of ZnO-based photocatalysts, addressing challenges associated with narrow bandwidth absorption and limited reactivity, and advancing the development of sustainable and effective environmental remediation technologies [310-313].

4.4 Challenges, Limitations, and Future Directions

4.4.1 Photocatalyst recovery and reuse

Photocatalyst recovery and reuse strategies play a pivotal role in enhancing the sustainability and economic feasibility of photocatalytic processes. Following the degradation of contaminants, the recovery of photocatalysts like zinc oxide (ZnO) is crucial to minimize operational costs and reduce environmental impact. Filtration, centrifugation, or magnetic separation methods are often employed to isolate and recover photocatalytic nanoparticles from the reaction mixture. Once recovered, the photocatalyst can be regenerated through washing and drying processes, restoring its activity for subsequent use. The ability to reuse photocatalysts not only conserves resources but also contributes to the overall efficiency of the photocatalytic system, making it more attractive for large-scale applications in water treatment, air purification, and other environmental remediation processes. Additionally, strategies for efficient recovery and reuse align with the principles of green chemistry, promoting sustainable practices in the field of advanced oxidation technologies [314-317].

4.4.2 Large-scale application and process integration

The large-scale application and process integration of advanced photocatalysts, such as zinc oxide (ZnO), are critical considerations in deploying efficient and sustainable environmental remediation technologies [318-320]. Scaling up photocatalytic processes for applications like water treatment and air purification involves optimizing reactor design, ensuring uniform illumination, and addressing challenges associated with catalyst recovery and reuse. Process integration with existing industrial systems is essential for practical implementation, requiring considerations of compatibility, adaptability, and energy efficiency. The successful large-scale application of photocatalysts often involves collaborative efforts between researchers, engineers, and industry stakeholders to develop integrated systems that meet regulatory standards, minimize environmental impact, and address the diverse challenges posed by real-world applications. By bridging the gap between laboratory-scale experiments and industrial deployment, the large-scale application and process integration of advanced photocatalysts contribute to the realization of sustainable and effective solutions for environmental challenges on a global scale [321-324].

4.4.3 Addressing incomplete degradation and secondary pollution

Addressing incomplete degradation and mitigating the risk of secondary pollution is a paramount concern in the application of advanced photocatalysts, such as zinc oxide

(ZnO), for environmental remediation. While photocatalysis is effective in breaking down organic pollutants, the potential formation of partially degraded intermediates or byproducts raises concerns about the overall environmental impact. Strategies to overcome incomplete degradation involve optimizing reaction conditions, catalyst dosage, and irradiation time to ensure comprehensive pollutant breakdown. Additionally, the integration of complementary treatment methods, such as advanced oxidation processes or post-treatment steps, can be employed to further enhance the overall efficiency and address any residual pollutants. Balancing the efficacy of degradation with the prevention of secondary pollution is crucial in developing sustainable and environmentally benign applications of photocatalytic technologies, emphasizing the importance of comprehensive research and strategic process design to minimize the unintended consequences of incomplete pollutant transformation [325-327].

4.4.4 Future research areas and emerging technologies

Future research in the realm of Optimization Strategies for Enhanced Degradation should focus on exploring innovative techniques and emerging technologies to improve the efficiency and sustainability of degradation processes. Advanced optimization algorithms, machine learning models, and data-driven approaches can be leveraged to optimize degradation pathways, enhance reaction kinetics, and minimize undesired byproducts. Additionally, the integration of cutting-edge technologies such as nanotechnology, biotechnology, and materials science holds promise for developing novel materials and catalysts that can significantly boost degradation rates. The exploration of synergistic approaches, combining various optimization strategies, is crucial to address the complex and multifaceted nature of degradation processes, paving the way for more effective and environmentally friendly solutions in waste management and pollutant remediation [328-330].

5. Conclusions and Recommendations

5.1 Overview of the current state of ZnO-based photocatalytic degradation of azo dyes

The current state of ZnO-based photocatalytic degradation of azo dyes represents a dynamic and promising field in environmental remediation. Zinc oxide (ZnO) photocatalysts have gained considerable attention due to their unique properties, such as high photoactivity and chemical stability. In the realm of azo dye degradation, ZnO-based photocatalysis has demonstrated efficient removal of these challenging pollutants through the generation of reactive oxygen species upon exposure to UV or visible light. The photocatalytic process involves the transfer of photoinduced electrons and holes, leading to the formation of highly oxidative species that break down azo dyes into less harmful substances. Challenges still exist, including issues related to catalyst reusability, scalability, and selectivity. Nevertheless, ongoing research efforts are focused on addressing these challenges and further optimizing ZnO-based photocatalytic systems for azo dye degradation, with the ultimate goal of developing sustainable and effective approaches for water and wastewater treatment.

5.2 Implications for industrial application and environmental management

The implications for industrial application and environmental management stemming from the ZnO-based photocatalytic degradation of azo dyes are substantial and hold significant promise. The efficient removal of azo dyes through ZnO photocatalysis presents a viable and environmentally friendly solution for wastewater treatment in

various industries, particularly those involved in textile and dye manufacturing. Implementation of this technology can contribute to reducing water pollution and meeting stringent environmental regulations. The scalability and adaptability of ZnO-based photocatalysis make it a potential candidate for large-scale industrial applications. However, the successful integration of this technology into industrial processes requires addressing challenges related to catalyst stability, reusability, and cost-effectiveness. Furthermore, the environmentally benign nature of ZnO photocatalysis aligns with the broader goals of sustainable environmental management, offering a promising avenue for mitigating the impact of azo dyes on ecosystems and human health. As research in this area progresses, the insights gained can inform policy decisions and foster the adoption of cleaner technologies for effective environmental stewardship.

5.3 Recommendations for overcoming current challenges and gaps in knowledge

To overcome current challenges and address gaps in knowledge within the realm of ZnO-based photocatalytic degradation of azo dyes, several recommendations can be considered. First and foremost, there is a need for intensified research efforts to enhance the understanding of the fundamental mechanisms governing ZnO photocatalysis in azo dye degradation. This includes a detailed exploration of the factors influencing catalyst stability, photoactivity, and selectivity under diverse environmental conditions. Additionally, collaborative interdisciplinary research endeavors between materials scientists, environmental engineers, and chemists could facilitate the development of advanced ZnO-based photocatalysts tailored for specific azo dye pollutants. Furthermore, investigations into catalyst immobilization techniques, such as nanocomposite materials or supported ZnO structures, could enhance catalyst recyclability and overall efficiency. Standardization of experimental methodologies and the development of benchmarking criteria would contribute to the comparability of results across different studies. Ultimately, a holistic approach that considers not only the technical aspects but also economic feasibility and environmental impact assessments will contribute to the successful translation of ZnO-based photocatalysis from the laboratory to practical and sustainable industrial applications.

5.4 Suggestions for future research directions

Future research in the field of ZnO-based photocatalytic degradation of azo dyes should explore novel avenues to advance the efficacy and applicability of this technology. Firstly, investigating the synergistic effects of ZnO with other photocatalytic materials or nanocomposites could enhance overall performance and address existing limitations. Understanding the role of different operational parameters, such as pH, temperature, and dye concentration, is crucial for optimizing the photocatalytic process. Exploring alternative light sources, including visible light, and evaluating their impact on ZnO photocatalysis can broaden the scope of its application. Furthermore, comprehensive studies on the fate of intermediate products and potential toxicity during azo dye degradation will provide valuable insights for environmental risk assessment. The development of efficient catalyst recovery and reuse strategies, along with a focus on the scalability of the process, will contribute to its practical implementation in wastewater treatment. Additionally, a more comprehensive life cycle assessment considering the environmental impact and economic feasibility of ZnO-based photocatalysis should be integrated into future research agendas, promoting a holistic and sustainable approach to azo dve remediation.

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