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EDITED BY
Tshimangadzo Munonde,
University of South Africa, South Africa

REVIEWED BY
Neeraj Kumar,
Council for Scientific and Industrial Research (CSIR), South Africa
Masixole Sihlahla,
University of Johannesburg, South Africa

*CORRESPONDENCE
Nyiko M. Chauke,
nyikoc@mintek.co.za

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Harnessing visible light: enhancing TiO_2 photocatalysis with photosensitizers for sustainable and efficient environmental solutions

Nyiko M. Chauke*, Reagan L. Mohlala, Siphelo Ngqoloda and Mpfunzeni C. Raphulu

Catalysis Group, Advanced Material Division, Mintek, Randburg, South Africa

The emerging field of using titanium dioxide (TiO_2)-based photosensitizers for enhancing photocatalytic removal of thiazine dyes such as methylene blue (MB) from water has long been recognized for its exceptional photocatalytic properties, making it an attractive material for environmental remediation and energy conversion. However, its wide bandgap limits its responsiveness to visible light. As such, the utilization of TiO_2-based photosensitizers for the removal of thiazine dyes, presents a promising avenue for diverse applications. In addressing the dual challenges of environmental pollution and harnessing sustainable energy sources, this review focuses on the removal of thiazine dyes from water and their subsequent application as photosensitizers for TiO_2 materials. Thiazine dyes, ubiquitous in industrial effluents, pose environmental concerns due to their persistence and potential toxicity. Conversely, this innovative approach involves employing TiO_2 materials as photocatalysts, utilizing the unique properties of thiazine dyes to enhance light absorption. Studies have shown that beyond the conventional role of thiazine dyes as colorants, they can serve as effective photosensitizers when coupled with TiO_2. This tandem not only facilitates the elimination of thiazine dyes, such as MB, from water but also augments the improvement of the photocatalytic performance of TiO_2 materials. The synergy between dye sensitizers and TiO_2 enhances the overall efficiency of processes like dye degradation and water splitting. Dye sensitizers, acting as light energy absorbers, can efficiently transfer this energy to TiO_2, thereby promoting electron transfer and generating reactive oxygen species (ROS). These ROS, in turn, initiate chemical reactions, rendering dye sensitizers valuable in applications such as wastewater treatment, solar energy conversion, and environmental remediation. As such, it is crucial to acknowledge the potential drawbacks associated with thiazine dyes, including toxicity and non-biodegradability. Consequently, careful consideration must be given to thiazine dye application and disposal. Therefore, this review manuscript delves into the comprehensive exploration of TiO_2-based photosensitizers, shedding light on their efficacy in various photocatalytic processes for thiazine dye removal.

KEYWORDS

titanium dioxide (TiO_2), thiazine dyes, photosensitizers, photocatalysis, visible light, hybrid materials, photodegradation, water treatment

1 Introduction to TiO_2 as a photocatalyst

Photocatalysis, a phenomenon that harnesses the power of light to drive chemical reactions on the surface of semiconductors, has garnered substantial attention in the realm of environmental and energy-related research (Magalhães et al., 2017; Tahir et al., 2020; Li et al., 2020). Among the diverse array of photocatalysts, titanium dioxide (TiO_2) has emerged as a paradigmatic and widely studied material due to its exceptional photochemical properties and versatile applications (AlSalka et al., 2023). This review delves into the multifaceted aspects of TiO_2 photocatalysis, emphasizing its significance, its inherent limitations concerning visible light utilization, and the pivotal role played by photosensitizers such as thiazines in augmenting TiO_2 photocatalytic efficacy.

TiO_2 photocatalysis is a photochemical process that exploits the semiconducting properties of this material to catalyze a myriad of chemical reactions when exposed to ultraviolet (UV) or visible light irradiation (Schneider et al., 2014; Pendergast et al., 2010). Its significance lies in the potential to address a wide spectrum of global challenges, ranging from environmental remediation to renewable energy technologies (Zhang et al., 2022). The pioneering work of Akira Fujishima and Kenichi Honda in the late 1960s brought TiO_2 photocatalysis to the forefront by showcasing its ability to split water into hydrogen and oxygen when illuminated by UV light, thereby initiating the exploration of TiO_2 as a photocatalyst for water splitting and pollutant degradation (Kenichi Honda, 2023; Fujishima and Honda, 1972). TiO_2 photocatalysis has since emerged as a sustainable and eco-friendly strategy for mitigating environmental pollution. Its ability to mineralize a variety of organic pollutants into harmless by-products has made it an invaluable tool for wastewater treatment and air purification (Schneider et al., 2014; Dharma et al., 2022). The ability to harness solar energy for these processes has the potential to revolutionize the energy landscape by offering an environmentally friendly alternative to conventional energy sources (AlSalka et al., 2023; Esrafili et al., 2022; Peiris et al., 2021). As a result, TiO_2 materials hold immense promise for the generation of clean energy through processes such as photocatalytic hydrogen production and photovoltaic applications.

Despite the myriad advantages of TiO_2, one of the most significant drawbacks as a semiconductor is the limited responsiveness to visible light, which constitutes a substantial portion of the solar spectrum. The intrinsic wide bandgap of TiO_2 (~3.2 eV for anatase and ~3.0 eV for rutile) only utilise UV light energy for the excitation of electrons from the valence band (VB) to the conduction band (CB) to enable photocatalytic reactions, which was reported by Anucha et al. (2022) and Rafique et al. (2020) in their studies (Anucha et al., 2022; Rafique et al., 2020). This limitation restricts the overall efficiency and practicality of TiO_2-based photocatalysis, as UV light comprises only a small fraction of the solar radiation reaching the Earth's surface (Anucha et al., 2022; Dong et al., 2015). This reliance on UV light not only limits the range of applications but also results in increased energy consumption for artificial UV light sources, diminishing the overall sustainability of the photocatalytic processes. To address these challenges and maximize the utilization of solar energy for photocatalysis, there is a compelling need to extend TiO_2 photoresponsiveness into the visible light region (Rafique et al., 2020; Dong et al., 2015). Through expanded light absorption, efficient charge separation, and improved catalytic activity, photosensitizers contribute to making TiO_2-based photocatalysis more versatile and effective for applications such as environmental remediation and solar energy conversion. A study by Tinoco et al. (2023) showed that TiO_2 is a widely used photocatalyst known for its ability to harness light energy to drive chemical reactions, particularly in the degradation of pollutants or the generation of clean energy (Tinoco Navarro and Jaroslav, 2023). As a result, incorporation of photosensitizers could play a crucial role in enhancing the photocatalytic activity of materials like TiO_2.

Anucha et al. (2022) have exhibited that the incorporation of photosensitizers is a strategy employed to address these limitations and improve the photocatalytic performance of TiO_2. The following are the key reasons why photosensitizers are important in the context of TiO_2 photocatalysis (Anucha et al., 2022). The TiO_2 primarily absorbs UV light due to its wide bandgap. Photosensitizers, on the other hand, can absorb light in a broader range, including visible light (Tinoco Navarro and Jaroslav, 2023; Yu et al., 2022). Through coupling a photosensitizer with TiO_2, the composite photocatalyst becomes capable of utilizing a wider spectrum of sunlight, making it more efficient under natural light conditions. The photosensitizers can facilitate the separation of photoinduced electron-hole pairs more effectively (Pawar et al., 2018). When light is absorbed by the photosensitizer, it generates an excited state with an electron at a higher energy level. This electron can then can be transfered to the conduction band of TiO_2, leaving behind a positive hole in the photosensitizer (Carella et al., 2018). This separation of charges helps to reduce electron-hole recombination rates, a common issue in TiO_2 photocatalysis that can limit its overall efficiency. In this regard, the presence of photosensitizers can boost the photocatalytic activity of TiO_2 by promoting specific reactions or pathways (Kang et al., 2019). For example, Shin et al. (2023) in their study showed that certain photosensitizers have been found to enable the generation of reactive oxygen species (ROS), which are highly effective in the degradation of organic pollutants (Shin et al., 2023). Such photosensitizers can also be engineered to have enhanced ROS generation by controlling their excitation wavelength. The formation of excited triplet states through intersystem crossing (ISC) plays a crucial role in the generation of ROS by organic photosensitizers (Wang et al., 2022). This showed that enhanced catalytic activity could contributes to the overall efficacy of TiO_2-based photocatalysts. Lastly, photosensitizers can modify the redox potential of TiO_2, making it more favorable for specific reactions. This modification can enhance the ability of TiO_2 to participate in oxidation-reduction reactions, which are often involved in photocatalytic processes (Kang et al., 2019; Al-Nuaim et al., 2022; Jiang et al., 2021).

2 TiO_2-based photosensitizers

Photosensitizers have emerged as a strategic solution to circumvent photocatalysts limitations such as wide band gap of TiO_2, ZnO, etc., regarding visible light utilization. These

TABLE 1 Summary of Dye photosensitizers used in TiO_2 modification.

Dye-sensitizer classification	Type of photosensitizer	Examples of Dye Materials	J_{SC} Range (mA cm^{-2})	Highest EFF (%)	Refs
Organic Dyes	Ruthenium Complexes	Ruthenium-based dyes, such as N_3 (cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)), have been extensively studied for DSSCs.	~14.13-18.14	7.42	Elmorsy et al. (2023)
	Cobalt Complexes	Some cobalt-based dyes have been investigated as alternatives to ruthenium-based dyes.	~0.12-4.40	2.49	Hegde et al. (2023)
	Natural Dyes	Dyes extracted from natural sources, such as chlorophyll, anthocyanins, and other plant pigments, have been used as eco-friendly alternatives.	~2.76-3.39	0.84	Amogne et al. (2020)
Inorganic Dyes	Perovskite Materials	Certain perovskite materials have been explored as sensitizers for TiO_2-based DSSCs.	~0.74	0.27	Sinha et al. (2019)
	Quantum Dots	Quantum dots, such as CdSe and PbS, have been investigated as potential sensitizers due to their tunable optical properties.	~8.98-12.22	2.35	Justin Raj et al. (2014)
Metal-Free Organic Dyes	Organic Sensitizers	Some metal-free organic dyes, such as porphyrins, squaraines, and organic polymers, have been developed for TiO_2 sensitization.	~5.92-8.85	5.87	Lee et al. (2018)
Transition Metal Complexes	Copper Complexes	Copper-based dyes have been studied for DSSCs.	~0.4-5.2	2.44	Jilakian and Ghaddar (2022)
	Cobalt Complexes	Besides cobalt complexes mentioned earlier, other cobalt-based dyes have been explored.	~0.06-0.22	25	Ursu et al. (2024)
Dye Design and Engineering	Molecular Engineering	Researchers have focused on designing and engineering dye molecules to optimize their absorption spectra, electron injection efficiency, and stability.	~7.10-8.30	10.88	Liu et al. (2023)
Co-Sensitization Strategies	Co-Sensitization	Combining different dyes to create a co-sensitization system has been explored to enhance light absorption across a broader spectral range.	~3.71-17.02	8.15	Ananthakumar et al. (2019)
Anchor Groups and Linkers	Functional Groups	The type of anchoring group and linker used in the dye molecule plays a crucial role in adsorption onto the TiO_2 surface and electron injection efficiency.	~0.79-1.03	0.42	Zhang and Cole (2015)
Electrolyte Systems	Redox Mediators	The choice of redox mediators in the electrolyte system also influences the performance of TiO_2-based DSSCs.	~4.17-12.59	4.76	Hu et al. (2019)

molecular entities, which can absorb visible light, subsequently transfer their photoexcited electrons to TiO_2, extending its absorption spectrum into the visible region (Hamza et al., 2023; Escudero et al., 2021). This energy transfer mechanism facilitates the excitation of TiO_2 electrons from the valence band to the conduction band, enabling the photocatalytic process to occur under visible light irradiation. Incorporating photosensitizers into TiO_2-based photocatalytic systems has become a pivotal strategy to enhance the efficiency and versatility of TiO_2 photocatalysis. Photosensitizers may encompass a diverse range of compounds, including organic dyes, metal complexes, and semiconductor quantum dots, each possessing unique optical and electronic properties that can be tailored to specific photocatalytic applications (AlSalka et al., 2023; Esrafili et al., 2022; Anucha et al., 2022; Sakar et al., 2019). TiO_2 is a widely used semiconductor material in the field of dye-sensitized solar cells (DSSCs) where it serves as the photoanode, and its surface is sensitized with a dye to enhance light absorption and electron injection. Various dyes have been developed over the years for this purpose. Table 1 generally summaries typical dye photosensitizers used to modify TiO_2 material.

As shown on Table 1, dye photosensitizers exhibited a remarkable performance by efficiently harnessing light energy to initiate intricate photochemical processes, facilitating enhanced charge carrier generation and separation for applications ranging from photocatalysis to sustainable environmental technologies. As a result, researchers continue to explore novel dye structures and sensitization strategies to improve the efficiency and stability of TiO_2-based photosensitizers. The judicious selection and design of photosensitizers have thus opened up new horizons for harnessing visible light and expanding the scope of TiO_2 photocatalysis, allowing for more sustainable and energy-efficient processes (Liu et al., 2023; Wategaonkar et al., 2021). Therefore, TiO_2 photocatalysis represents a powerful and versatile approach for addressing environmental and energy challenges. However, its limited responsiveness to visible light has prompted the integration of photosensitizers as a strategic means to enhance its photocatalytic activity. This comprehensive review explores the

multifaceted aspects of TiO_2-based photosensitizers for the removal and reuse of thiazine dyes such as MB from water, shedding light on their synthesis, characterization, and applications in diverse photocatalytic processes, thereby advancing the field of sustainable and efficient photocatalysis.

3 Thiazine dyes and their properties

Thiazines are classified as organic molecules, which can be structured in many different ways, as shown in Figure 1. In organic synthesis, thiazines are produced from the reaction of thiourea and alkyl propiolates compounds (Danilkina et al., 2006; Begum Sri Padmavati Mahila Visvavidyalayam et al., 2016; Mohlala et al., 2021; Pirillo et al., 2018). These groups of organic compounds have been extensively explored in the literature for diverse applications, spanning biological activities and material utilization. Although thiazine dyes are considered toxic, they find application as photosensitizers in pharmaceutical applications.

In the absence of light, thiazine dyes remain non-toxic. However, upon exposure to an appropriate amount of light, they undergo a transformation, becoming highly reactive (Mohlala et al., 2021; Pirillo et al., 2018; Fabio et al., 2016). Thiazine dyes are among the most significant organic dyes with established uses in technology and science. They are employed in a variety of chemical, biological, and medical research studies (Gilani et al., 2017). Because of their acceptable biological, chemical, photochemical, and photophysical properties, these cationic dyes are utilized as phototherapeutic agents. The physiological and physicochemical characteristics of the thiazine dyes influences the effectiveness of the photodynamic therapy (PDT). To date the generation of thiazine dyes as photosensitizers in the presence of light is driven to improve properties such as cytotoxicity, chemical purity and composition (Montes De Oca et al., 2013). These set of compounds are also derived to be effective in the production of singlet oxygen, photochemical reactivity, high extinction coefficient and referential retention by the target tissue (Robertson et al., 2009; Detty et al., 2004; Triesscheijn et al., 2006). The high singlet oxygen quantum yields of thiazine dyes contribute to their efficacy in inducing photodynamic reactions. This feature is particularly advantageous for the degradation of organic pollutants present in wastewater.

Global production of various dyes amounts to over 700,000 tons per year, and the textile dye sector generates significant amounts of highly coloured wastewater from dye processes (Eslami et al., 2015). Since all of this wastewater is poisonous and has the potential to be dangerous, it should be cleaned up before being dumped into rivers, streams, or the ocean (Cunico et al., 2015). Table 2 provides an overview of various thiazine dyes along with key properties relevant to their application in photocatalysis and environmental processes. The included dyes encompass a range of well-known compounds, each distinguished by its unique chemical structure, absorption wavelength, photocatalytic activity, and environmental impact.

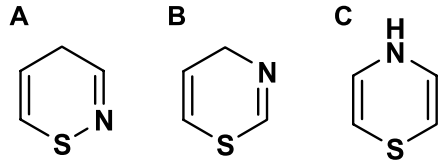


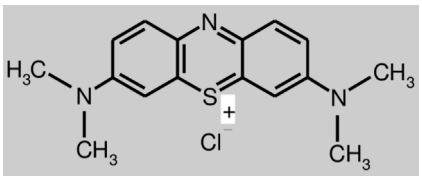
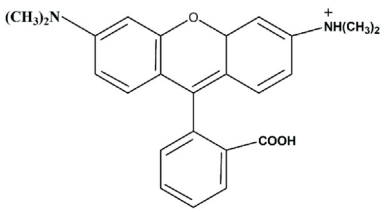
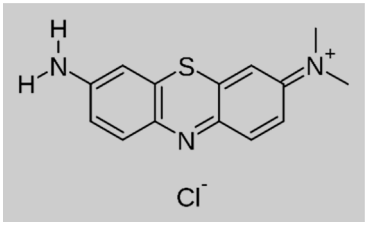
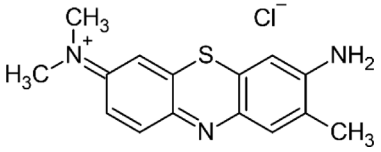
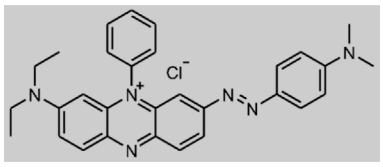
FIGURE 1
Structures of 1,2- **(A)**, 1,3- **(B)** and 1,4- **(C)** thiazine.

The presented table offers a concise overview of various thiazine dyes. Methylene Blue, with its high photocatalytic activity at a 665 nm absorption wavelength, emerges as a promising candidate (jie Song et al., 2023; Khan et al., 2022; Tardivo et al., 2005). Rhodamine B and Azure A exhibit moderate photocatalytic activity, while Toluidine Blue and Janus Green B show varying degrees of effectiveness. The choice of thiazine dye in photocatalysis is multifaceted, considering factors like absorption wavelength, environmental impact, and overall performance. Rhodamine B and Toluidine Blue, despite moderate photocatalytic activity, may find applications in scenarios where a balance between performance and environmental impact is critical (Hamza et al., 2023; Valadez-Renteria et al., 2022). Furthermore, continuous exploration and understanding of the chemical structures and properties of thiazine dyes will contribute to the optimization of photocatalytic processes and the development of sustainable environmental technologies.

The majority of dyes have stable chemical structures that ae challenging to break down; in particular, azo and cationic thiazine variants, which are produced in vast quantities, and are most challenging (Navarro et al., 2017). Treatments for the degradation of azo and cationic thiazine dyes employing several advanced oxidation processes (AOPs) have garnered a lot of attention lately (Luo et al., 2017). Research on wastewater treatment for the degradation of household wastes, agricultural discharges, and industrial effluents has been conducted for a long time. To identify and illuminate the hazardous emergence from the pollutants, the plant needs its initial detection system. The sludge extraction process reverses osmosis, membrane filtration, photocatalysis, and flocculation are some of the cutting-edge techniques for treating wastewater introduced by nanotechnology (Asahi et al., 2001). According to a report, TiO_2 and ZnO nanostructures are employed as efficient photocatalysts for the treatment of wastewater because they possess many advantages, which include high activity, affordability, stability, and nontoxicity (Bhatkhande et al., 2002).

Photocatalysis has emerged as a well-organized method for air and water purification through the degradation of contaminants that are commonly used in organic colorants on paper, plastics, food, leather, textiles, and cosmetics. Because the effluents maximize chemical oxygen demand, they are highly dangerous to aquatic environments and species (Murray and Parsons, 2004). Since the majority of organic dyes are both stable and resistant to photodegradation, currently research is being done on the removal of these released dyes. However, in typical wastewater treatment, thiazine dye removal or incorporation into the photocatalysts can in turn be tailored to selectively and further target specific contaminants commonly found in wastewater, such as organic matter, microbes, and other impurities. This selectivity could minimize the impact on non-target components, ensuring a more focused and efficient treatment process as well as the reuse of thiazine dyes. As a result, the use of thiazine dyes as photosensitizers

TABLE 2 Overview of thiazine dyes and their photocatalytic properties.

Thiazine Dye	Chemical Structure	Absorption Wavelength (nm)	Photocatalytic Activity	Environmental Impact
Methylene Blue		665	High	Moderate
Rhodamine B		554	Moderate	Low
Azure A		631	High	Moderate
Toluidine Blue		630	Moderate	Low
Janus Green B		640	Low	Low

in wastewater treatment presents a future prospect that can lead to their reduced environmental footprint. Their low toxicity to healthy organisms and tissues could make them a more sustainable alternative compared to traditional water treatment chemicals (Zhang et al., 2023).

In addition, the thiazine compounds ability to self-assemble has significant implications for a variety of applications, including photo-medicine, fluorescence depolarization diagnostics, tunable lasers, molecular optoelectronics, and photographic technologies (Arik and Onganer, 2003). Thiazine dyes are more stable in aqueous solutions as they do not undergo demethylation (Abbott, 1962) and they have low ionization potential due to the presence of two heteroatoms, which could limit their toxicity in water (Havelcovaâ et al., 2023). Intrinsically thiazine set of compounds are ideal candidates for photodynamic treatment because they exhibit selectivity for cancer cells *in vivo* (Paul and Suresh Kumar, 2013) and have high singlet oxygen quantum yields (Ronzani et al., 2014). Thiazine dyes as photosensitizers have also shown to have antibacterial effects on a variety of harmful microbes, which could be also beneficial in wastewater treatment (Pinto et al., 2017; Decker et al., 2017; Monteiro et al., 2017). However, it effectiveness as a dye photosensitizer for wastewater treatment is still an unproven hypothesis. Meanwhile, despite these benefits of thiazine dyes, it is well known that their planar and even ionic structures tend to congregate in diluted fluids, producing dimers and occasionally higher-order aggregates (Chakraborty et al., 2010; Dar and Ankari, 2022). This phenomenon is mainly associated with the hydrophobic character of the basic structure of thiazine dyes (Gilani et al., 2017).

On the other prospect, the removal of thiazine dyes, particularly methylene blue, from wastewater has gained significant attention, and TiO_2-based photosensitizers have emerged as effective agents. When combined with TiO_2, thiazine dyes like MB can serve as potent photosensitizers, enhancing the photocatalytic activity of TiO_2 and enabling the efficient removal of these dyes from water (Khan et al., 2022; Kohle et al., 2020; Basumatary et al., 2022). However, the interaction between thiazine dyes and TiO_2 involves the absorption of light energy by the dyes, which is then transferred to TiO_2. This process promotes electron transfer and the generation of ROS, which play a

pivotal role in initiating chemical reactions (Sarfraz et al., 2023; Rao et al., 2022; Lima and Reis, 2023). The photocatalytic activity induced by TiO_2-based photosensitizers proves valuable in the degradation of thiazine dyes, contributing to the remediation of wastewater. This environmentally friendly approach not only addresses the removal of pollutants but also aligns with the broader goals of sustainable water treatment technologies. The integration of TiO_2-based photosensitizers for thiazine dye removal and reuse holds promise for advancing efficient and eco-friendly wastewater treatment strategies.

4 Light absorption and energy transfer by photosensitizers

The mechanisms of light absorption and energy transfer between dye sensitizers and TiO_2 involve a series of intricate steps that facilitate the enhancement of photocatalytic activity. For example, organic dye, as a photosensitizer, absorbs light energy, typically in the visible spectrum (Zani et al., 2021). This absorbed energy excites the electrons within the dye molecules to higher energy states. Subsequently, the excited electrons in organic dye are transferred to the TiO_2 surface through a process known as energy transfer. TiO_2, being a semiconductor, effectively captures and utilizes the transferred electrons (Zani et al., 2021; Zhao et al., 2021).

The interaction between dye sensitizers and TiO_2 is governed by the creation of electron-hole pairs on the TiO_2 surface upon absorbing the transferred electrons. This process promotes efficient charge separation, where electrons move through the TiO_2 lattice while holes are left behind (Elmorsy et al., 2023; Zani et al., 2021). The excited electrons on the TiO_2 surface can participate in redox reactions, leading to the generation of ROS, such as superoxide ions and hydroxyl radicals. These ROS play a crucial role in initiating chemical reactions and promoting the degradation of organic pollutants, including the thiazine dyes. The synergistic interaction between photosensitizers and TiO_2 amplifies the photocatalytic activity of TiO_2, making it a powerful approach for applications such as wastewater treatment and dye degradation (Elmorsy et al., 2023; Ananthakumar et al., 2019).

4.1 Photosulfitochemistry mechanism of MB dye

A study by Luo et al. (2021) reported the photosulfitochemistry mechanism of MB dye as demonstrated in Figure 2. The mechanism outlines a sequence of chemical reactions involved in the wastewater treatment process using MB as a photosensitizer involving five processes namely;

(i) Photo-excitation of MB^+: where the ground state MB^+ becomes excited to the single state $^1MB^{+*}$ after absorbing visible light. This process is followed by the generation of triplet state $^3MB^{+*}$ from $^1MB^{+*}$ after going through fast intersystem crossing (ISC). For the sake of simplicity in this process, the ISC reaction is not included here, and MB^{+*} stands for the excited MB^+'s triplet state.

(ii) Electron transfer between MB^{+*} and sulfite: When MB^{+*} removes an electron from sulfite, primary radicals $MB^•$ and SO_3^{-} are created. At this point, the oxysulfur radical chain reaction is currently at its starting phase.

(iii) Radical propagation: After reacting with an oxygen molecule to generate secondary highly oxidative SO_5, SO_3^{-} next interacts with sulfite to form SO_4^{-}.

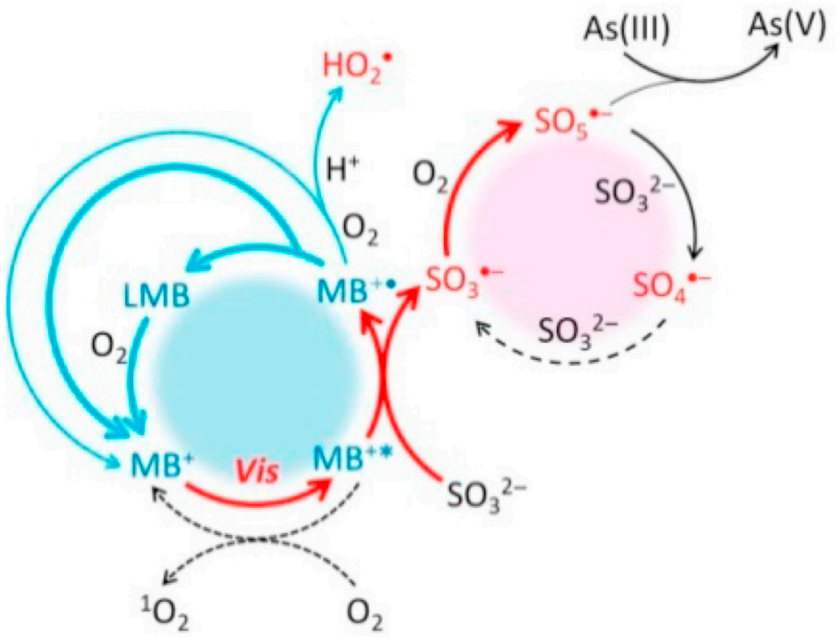


FIGURE 2
The As(III) oxidation mechanism in the photo-MB^+-sulfite system at neutral pH (Luo et al., 2021).

(iv) Recovery of MB^+: MB^+ recovery is achieved by the radical termination of $MB^{\bullet}$ *via* disproportionation or radical transfer to oxygen. As an intermediate from the disproportionation of $MB^{\bullet}$, the colourless dye Leuco methylene blue (LMB) is readily reoxidized by O_2 back to MB^+. When compared to transition metals as a catalyst for sulfite activation, MB^+/LMB exhibits a substantially faster redox turnover, which facilitates a significant As(III) oxidation and requires significantly less MB^+ concentration.

(v) As(III) oxidation: The primary radical oxidant that causes As(III) oxidation is $SO_5^{\bullet-}$.

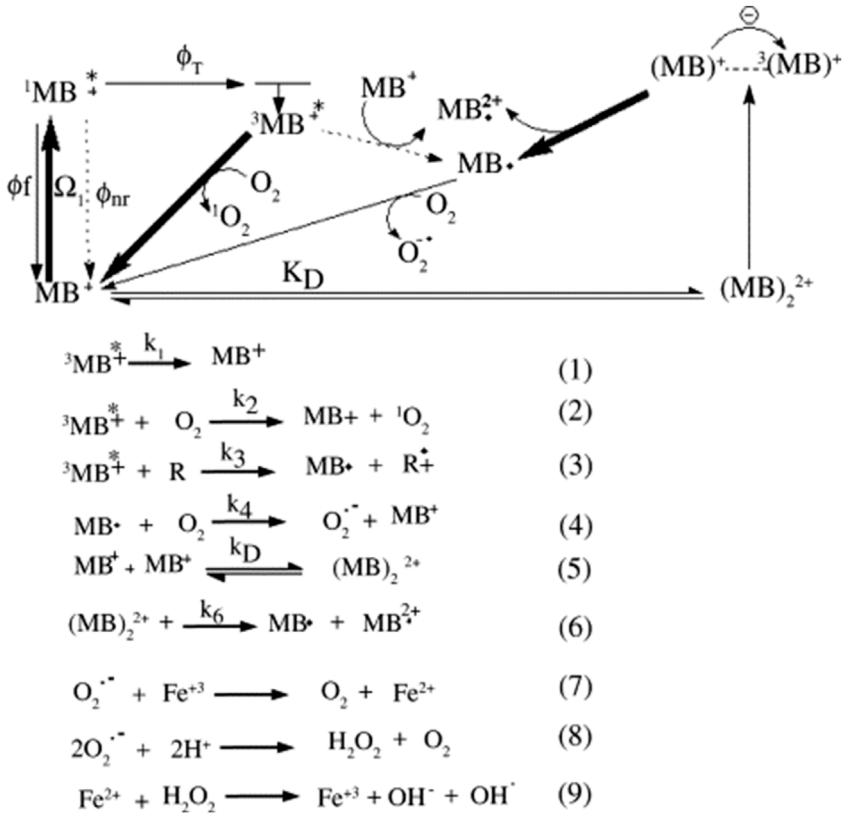
As a result, the use of $MB^{\bullet}$ and its recovery in this process is advantageous due to its faster redox turnover compared to transition metals as catalysts for sulfite activation. This efficiency facilitates significant As(III) oxidation and requires lower $MB^{\bullet}$ concentrations (Luo et al., 2021). Intrinsically, it is worth noting that the overall success of this wastewater treatment process depends on factors such as reaction kinetics, efficiency of radical generation, and the ability to recycle thiazine dyes i.e., MB effectively. Additionally, the specifics of the ISC reaction and any possible side reactions not mentioned may influence the overall performance of the system. Notably, MB has been widely employed in the photooxidation of both synthetic and natural compounds (Tardivo et al., 2005; Luo et al., 2021; Yhon et al., 2023). As shown on Scheme 1, two main types of photochemical process can be observed, which can be explained as follows:

Type I, is where reducing agents gives an electron to the MB triplet, generating the semi-reduced radical MB, Reaction (3), in Scheme 1, and Type II, is where the triplet energy is transferred to oxygen, forming singlet oxygen ($^1O_2$, Reaction (2)) (Scheme 1). The ground state MB molecules can function as reducing agents by themselves at high dye concentrations (D – D* mechanism) (Junqueira et al., 2002; Severino et al., 2003). As such, the schematic representation demonstrates the effectiveness of using thiazines such as MB as photosensitizers.

Scheme 1 also shows the photochemical pathways for MB in which MB^+, $^1MB^{+*}$, $^3MB^{+*}$ represent the ground state, singlet, and triplet excited states of MB, respectively, which was reported by Tardivo et al. (2005) (Tardivo et al., 2005). In here, MB· and $MB^{\cdot 2+}$ represent the semi-reduced and semi-oxidized radicals of methylene blue, respectively; Ω_1 denotes light absorption; Φ_f, Φ_{nr}, Φ_T are fluorescence, non-radiative, and triplet quantum yield.

4.2 The mechanism of dye-sensitization process

The light that is typically applied in the visible and near-infrared wavelengths must stimulate photosensitizers in order to start the



SCHEME 1
The photochemical reaction pathways of methylene blue (Tardivo et al., 2005).

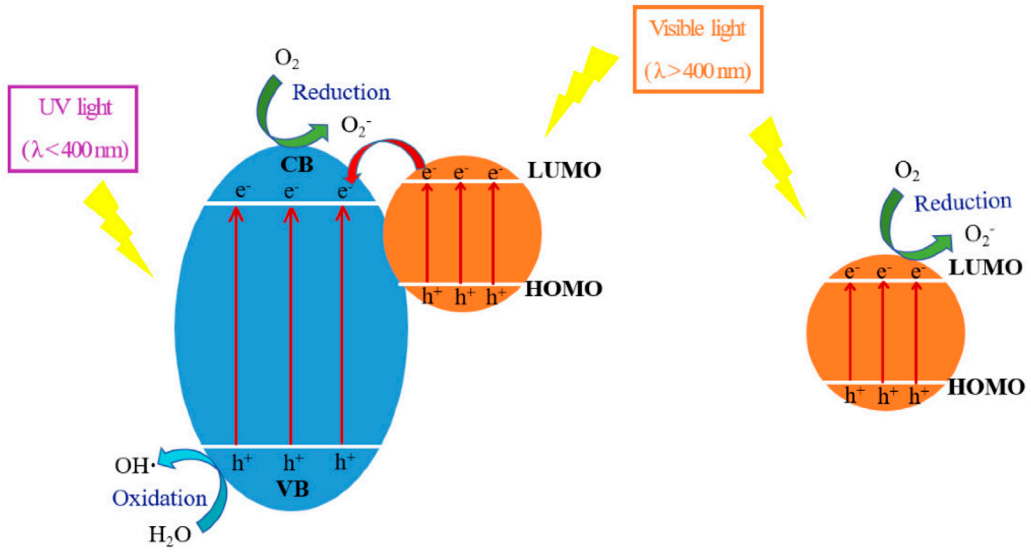


FIGURE 3
The mechanism of the dye sensitization process (Li et al., 2020).

photodynamic process. The initial state of the photosensitizer is a singlet state in which paired electrons in frontier molecular orbitals have opposing spins (Zhao et al., 2021; Li and Pu, 2019). Upon exposure to light of the appropriately designated wavelength, the photosensitizers absorb the light, resulting in the excitation of a single electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), while the spin remains unchanged during the process (Rossi, 2023; Kenry and Liu, 2022). When the photosensitizer is exposed to light with the right wavelength, it absorbs the light and one electron is excited from HOMO to the LUMO, with the spin staying unaltered throughout. This excited state, which lasts for only a few nanoseconds at most, is referred to as the excited singlet state (Rossi, 2023; Kenry and Liu, 2022; Huang et al., 2014). The photosensitization mechanism, as illustrated in Figure 3, involves electrons from the dyes HOMO excited to their LUMO and then injected to the CB of TiO_2. This process occurs once the dyes absorb photons in the visible light energy range of the solar spectrum (Li et al., 2020).

The occurrence of this excited singlet state is pivotal in initiating subsequent photochemical reactions and is fundamental to the overall functionality of photosensitizers in diverse applications such as photodynamic therapy, solar energy conversion, and photocatalysis (Zhao et al., 2021; Li and Pu, 2019; Xu et al., 2022; Monro et al., 2019). In this context, the singlet-excited state of photosensitizers can manifest in different pathways. It may either emit light in the form of fluorescence or undergo radiationless relaxation, converting the excitation energy into heat internally (Ortiz-Rodríguez et al., 2021). Alternatively, the excited electron has the option to reverse its spin, a process that, for most organic compounds, is relatively slow and requires a singlet state with an extended lifetime. The majority of organic compounds exhibit a prolonged lifetime for the singlet state due to the sluggish nature of the spin reversal process (Ortiz-Rodríguez et al., 2021; Stoll and Schweiger, 2006; Li et al., 2022). It is noteworthy that the excited electron, having a parallel spin relative to its unexcited, paired electron, transitions into the triplet state, which boasts a considerably longer lifetime. However, the return of the excited electron to the ground state in the triplet state is constrained by the Pauli exclusion principle, as this process is considered "spin forbidden" (Stoll and Schweiger, 2006; Li et al., 2022; Minaev et al., 2022). Consequently, the excited electron in the triplet state cannot simply revert to the ground level, leading to a substantially prolonged lifetime for the triplet state (Minaev et al., 2022). These intricate dynamics play a pivotal role in determining the fate of the excited state and influence the subsequent photochemical and photophysical processes in which the photosensitizer is involved. The triplet state is much longer lived because the excited electron possesses a parallel spin to its paired, unexcited electron. In the triplet state, the excited electron cannot easily fall back to ground level (a "spin forbidden" process such as this would violate the Pauli Exclusion Principle) (Ortiz-Rodríguez et al., 2021; Lynch et al., 2019).

4.3 Dynamics of photodynamic processes

The PDT exhibits its distinctive oxidative damage through the capability of photosensitizers to interact with oxygen during their prolonged triplet state. Exposure to light triggers electron-hole pairs in TiO_2, generating redox reactions that produce ROS, such as superoxide ions and hydroxyl radicals, which can damage organic pollutants in wastewater (Gilson et al., 2017). The extended triplet state of photosensitizers in PDT and the resulting oxidative damage pathways are analogous to the generation of ROS during the photocatalytic activity of TiO_2 in wastewater treatment (Tanielian et al., 2003). The corresponding pathways are illustrated in Figure 4, delineating the ensuing photochemistry and potential mechanisms of damage to various targets. In this process, the photosensitizer, residing in its triplet state with an extended lifetime, engages in interactions with molecular oxygen. This interaction initiates a cascade of events leading to the generation of ROS, such as singlet oxygen.

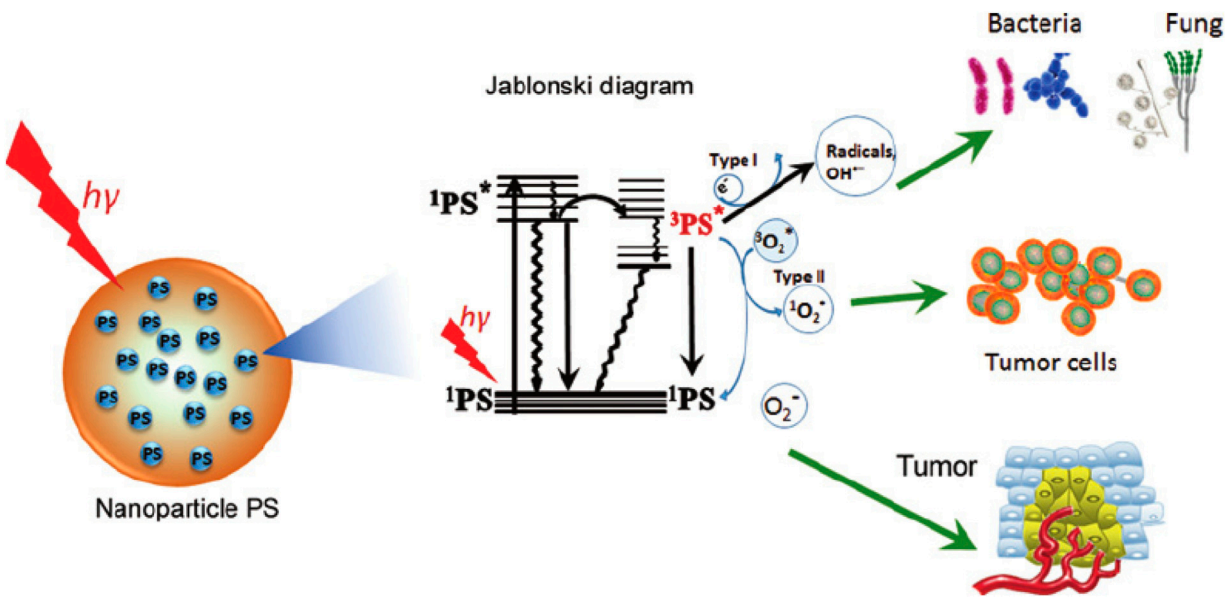


FIGURE 4
Photochemistry depicted in the Jablonski diagram (Das and Roychoudhury, 2014).

The ROS, particularly singlet oxygen, is highly reactive and can induce oxidative damage to biomolecules and cellular structures. These damaging effects are the basis for the therapeutic efficacy of PDT, as the targeted generation of ROS selectively damages cancer cells or other pathogenic targets (Das and Roychoudhury, 2014; Zapata et al., 2022; Abdal Dayem et al., 2017). The pathways depicted in Figure 4 provide a visual representation of the intricate photochemical processes and the subsequent mechanisms by which PDT induces oxidative damage to its intended targets (Das and Roychoudhury, 2014). Understanding these pathways is crucial for optimizing PDT protocols and expanding its applications in medical treatments and other fields. In the context of wastewater treatment, the oxidative damage caused by the extended triplet state of photosensitizers aligns with the oxidative degradation of pollutants facilitated by TiO_2 photocatalysis (Lima and Reis, 2023; Zhao et al., 2021). The pathways illustrated in Figure 4, along with the resulting photochemistry and potential mechanisms of damage to various targets, could be conceptually linked to the intricate processes involved in the photocatalytic degradation of contaminants in water using TiO_2 (Lima and Reis, 2023; Monro et al., 2019). Understanding these mechanisms aids in optimizing TiO_2-based photocatalysis for effective wastewater treatment and pollutant removal.

4.4 Mechanism of TiO_2-based photosensitization

The elucidation of photocatalytic mechanisms involving TiO_2-based dye photosensitizers is crucial for a comprehensive understanding of how these systems work and for optimizing their performance in various applications (Schneider et al., 2014; Sakar et al., 2019; Chen et al., 2020; Serpone, 2018). Researchers have employed a combination of experimental techniques and theoretical modelling to uncover these mechanisms. Figure 5 shows the mechanism of the dye sensitization process with the dye adsorbed onto the catalyst surface and dye in the bulk.

Thiazine dyes play a critical role in extending the light absorption range of TiO_2 (Rochkind et al., 2015; Bindhu et al., 2022). When exposed to light, thiazine dyes can absorb photons in the visible region, promoting electron excitation from their HOMO to their LUMO ground state to higher energy levels (Luo et al., 2021; Rochkind et al., 2015; Senthilkumar et al., 2010; Vara and Ortiz, 2016). Upon excitation, the thiazine dye molecules transfer electrons to the conduction band of TiO_2. This injection of photoexcited electrons into TiO_2 is facilitated by the difference in energy levels of the dye LUMO and the bandgap of TiO_2, particularly its CB position, and this is a key step in the photocatalytic process (Khan et al., 2022; Rochkind et al., 2015; Senthilkumar et al., 2010; Parrino et al., 2022; Ronca et al., 2012; Mezyen et al., 2023). The injected electrons can then participate in redox reactions on the surface of TiO_2 with adsorbed species or in the reduction of oxygen to form superoxide radicals. Simultaneously, when electrons are injected into the TiO_2 conduction band, holes (positive charge carriers) are created in the valence band of TiO_2 (Ronca et al., 2012; Elg et al., 2021). These holes can participate in oxidative reactions, such as the oxidation of water or organic pollutants, which is crucial for overall photocatalytic activity.

The efficiency of a TiO_2-based dye sensitizer system depends on the extent of charge separation and minimization of electron-hole recombination. Photogenerated electrons in the conduction band and holes in the valence band should be efficiently separated to avoid recombination, which would lead to a decrease in photocatalytic activity (Elmorsy et al., 2023; Zani et al., 2021). Photogenerated electrons and holes can interact with adsorbed species, leading to the formation of intermediate radicals. These radicals can participate in the degradation of organic pollutants or in other chemical reactions.

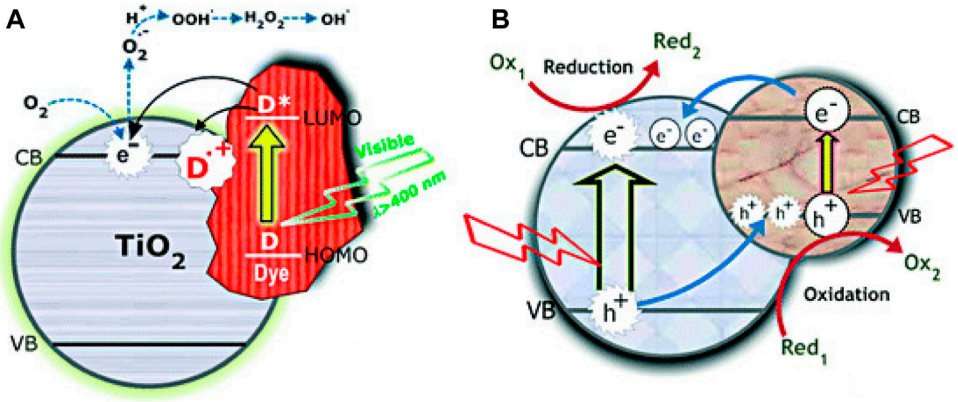


FIGURE 5
Mechanism of charge carrier transfer in semiconductor-coupled **(A)** narrow band gap TiO_2 and **(B)** dye-sensitized TiO_2 (Vinu and Madras, 2011).

For example, superoxide radicals formed from oxygen reduction can contribute to the degradation of organic compounds. Oxygen and water are often present in photocatalytic reactions. Oxygen can accept electrons from the conduction band, forming superoxide or other oxygen radicals. Water can serve as an electron donor to reduce holes in the valence band (Chakhtouna et al., 2021; Goodarzi et al., 2023; Humayun et al., 2022; Li et al., 2013). These reactions are crucial for pollutant degradation and hydrogen production.

4.5 Probing photocatalytic dynamics

The interaction of thiazine dye-sensitized TiO_2 with target molecules or pollutants on the surface is essential for the photocatalytic process (Zani et al., 2021; Senthilkumar et al., 2010; Barakat et al., 2022). Surface adsorption, electron transfer, and radical reactions play a significant role in the degradation or transformation of target compounds. Researchers often study the quantum yields of photocatalytic reactions to understand the efficiency of the process. Additionally, reaction kinetics are examined to determine rate constants, reaction pathways, and the role of intermediates (Senthilkumar et al., 2010; Araujo et al., 2022; Liu et al., 2014). To elucidate these mechanisms, researchers use techniques like transient absorption spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, surface science experiments, and computational modelling, including density functional theory (DFT) calculations (Qin et al., 2023). These methods provide valuable insights into the dynamic processes occurring during photocatalysis, helping to optimize TiO_2-based thiazine dye systems for various applications, including water treatment, pollutant degradation, and hydrogen production (Luo et al., 2021; Senthilkumar et al., 2010; Acar et al., 2015; Yang and Wang, 2018). Figure 6 demonstrates the application of EPR spectroscopy in $TiO_2$and Nb_2O_5 photocatalysis.

As shown in Figure 6, the application of EPR spectroscopy in the observation of paramagnetic centres formed upon irradiation of TiO_2 and niobium oxide (Nb_2O_5) photocatalysts was reported by Al-Madanat et al. (2021). They showed that electron paramagnetic resonance spectroscopy is a powerful technique that can be used to monitor the photoinduced phenomena occurring in semiconductors like TiO_2 and Nb_2O_5 photocatalysts. As such, the EPR spectroscopy provides precise insights into the dynamic and reactivity of the photocatalyst under different experimental conditions (Al-Madanat et al., 2021). It can characterize paramagnetic centers formed upon irradiation of these photocatalysts. The application of EPR in the observation of paramagnetic centers formed upon irradiation of TiO_2 and Nb_2O_5 photocatalysts has been studied. The EPR spectroscopy differentiates itself from other techniques by providing exceptional sensitivity and specificity towards species with unpaired electrons, including organic and inorganic radicals, crystal defects, dopant atoms, and both free and trapped charge carriers (Al-Madanat et al., 2021; Hurum et al., 2003). The results obtained from EPR spectroscopy can help in understanding the electron-hole recombination, the nature of trapped charge carriers, and the reactions involved in the photocatalytic process.

4.6 Electron and energy transfer processes

Electron and energy transfer processes are fundamental mechanisms that play a critical role in a wide range of scientific and technological applications, including photophysics, photochemistry, and photobiology (Parrino et al., 2022). Understanding these processes is essential for optimizing various technologies and advancing our knowledge of chemical and physical systems. Electron transfer refers to the movement of an electron from one molecular entity (donor) to another (acceptor). This process can be categorized into two types such as chemical electron transfer, where the transfer of electrons is accompanied by changes in the chemical structure of the donor and acceptor (Beranek, 2011; Bayard et al., 2021). This process is often observed in redox reactions, where the donor loses an electron (oxidation), and the acceptor gains an electron (reduction). Meanwhile, photoinduced electron transfer (PET) refers to a special case of electron transfer that occurs upon absorption of light by a photosensitizer (Beranek, 2011; Speirs et al., 2023). In this process, the excited photosensitizer (electron donor) transfers an electron to an acceptor molecule. The PET is essential in various

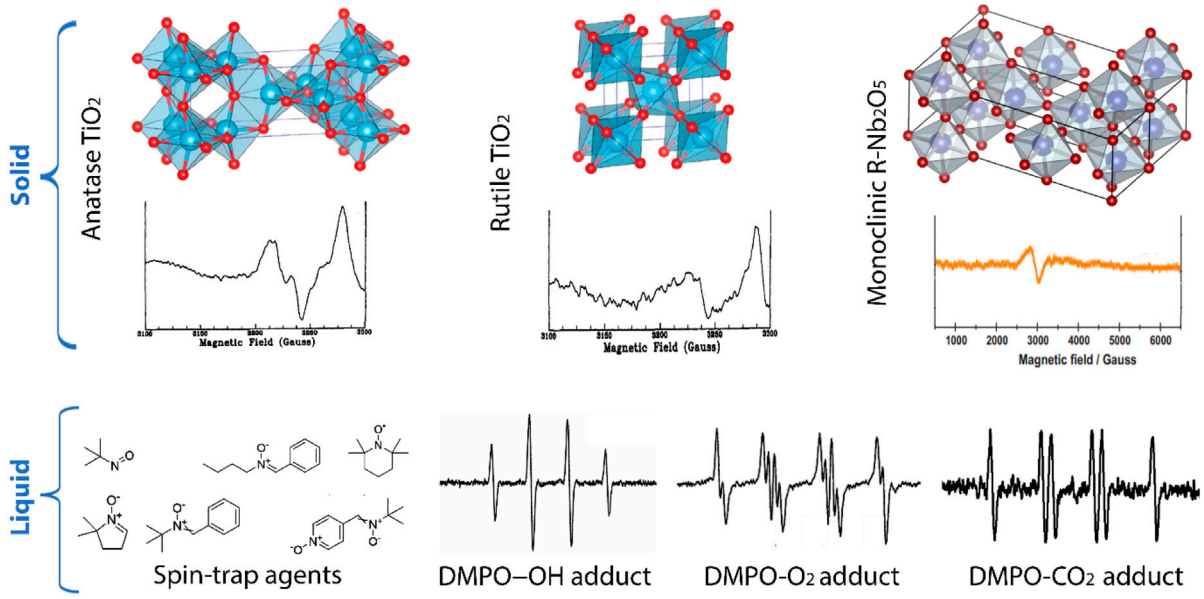


FIGURE 6
Application of EPR spectroscopy in TiO_2 and Nb_2O_5 photocatalysis (Al-Madanat et al., 2021).

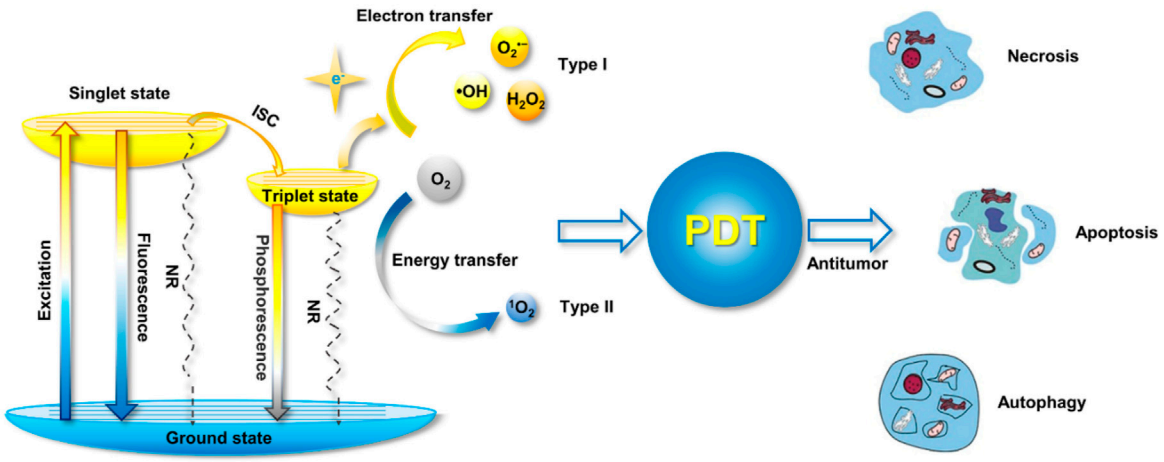


FIGURE 7
The Jablonski diagram shows the mechanism of ROS formation from photosensitizers, as well as the mechanisms underlying PDT-induced cell death (Yu et al., 2022).

photophysical and photochemical reactions, such as fluorescence quenching and charge separation in photovoltaic devices (Speirs et al., 2023; Buglak et al., 2022; El-Khouly et al., 2004). The photosensitization mechanism and the role of electron energy transfer in photosensitizers, including the generation of ROS and the potential for tuning ROS generation through anionization are shown in Figure 7.

As shown in Figure 7, the photosensitizers undergo excitation upon absorbing a photon, transitioning from the singlet ground state to a higher-energy state. In this regard, the energy is transferred from one molecular entity to another without an actual transfer of electrons. Hence, in photosensitizers, energy transfer occurs through the process of intersystem crossing (Yu et al., 2022). There are two main types of energy transfer, which are Radiative Energy Transfer (Forster Resonance Energy Transfer, (FRET)) and Non-Radiative Energy Transfer (Dexter Energy Transfer (DET)) (Calçada et al., 2019; Enhanced Photodynamic et al., 2022; van der Meer, 2013; Tavakkoli Yaraki et al., 2022). The FRET is an Radiative Energy Transfer process that occurs between two molecules (usually chromophores) nearby. When the energy levels of the donor and acceptor molecules are appropriately matched, energy can be transferred from the excited donor to the acceptor (Calçada et al., 2019; van der Meer, 2013). FRET is widely used in applications like fluorescence microscopy, molecular biology, and

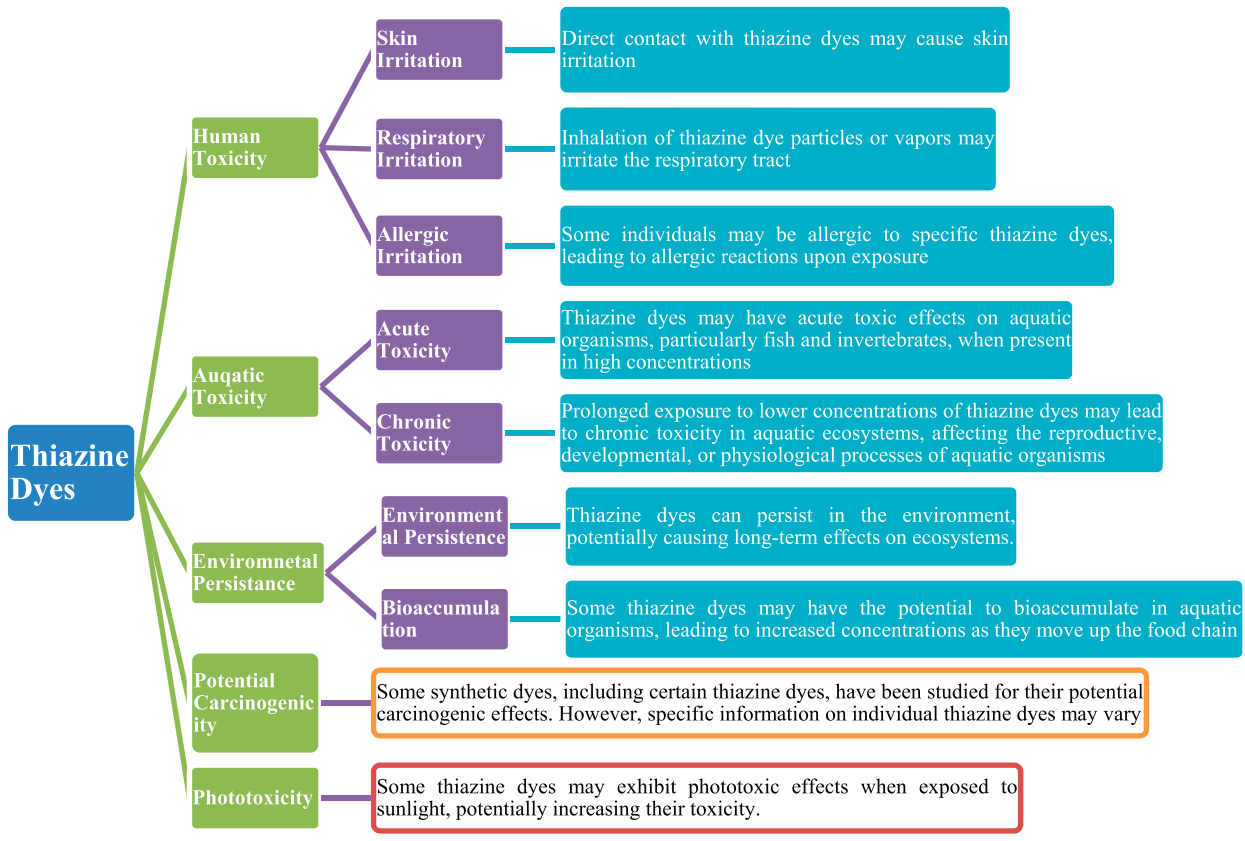
energy transfer-based sensors. While the dexter energy transfer is a non-radiative process, in which energy is transferred between molecules through electron-electron interactions without the emission of a photon (Chou and Dennis, 2015), (Sekar and Periasamy, 2003). As a result, this process is more distance-dependent than FRET and typically requires closer proximity between donor and acceptor molecules.

The rate and efficiency of both electron and energy transfer processes depends on various factors, such as the degree to which the electronic states of the donor and acceptor molecules overlap the distance between donor and acceptor, the solvent polarity, temperature, and surrounding conditions. The quantum yield represents the probability of a transfer event occurring and is a measure of the efficiency of the process (Sekar and Periasamy, 2003), (DeVine et al., 2015; Kubas, 2021; Roduner and Krüger, 2022). Electron and energy transfer processes are essential in many applications, such as light-harvesting systems in organic photovoltaic cells and solar panels, photoluminescence and fluorescent labelling techniques, sensors and probes for detecting molecular interactions and electron transport in biological systems, including respiration and photosynthesis (DeVine et al., 2015; Kaushal et al., 2023; Wang and Lu, 2022; Chen et al., 2015). Therefore, understanding and controlling electron and energy transfer processes have led to numerous technological advancements and continue to be areas of active research in chemistry, physics, and biology. These processes are crucial for the development of sustainable energy technologies, improved sensors and imaging techniques, and a deeper understanding of biological and chemical systems.

5 Advantages and disadvantages of using thiazine dyes as photosensitizers

5.1 Thiazine dye toxicity in water

Thiazine dyes are a class of synthetic organic dyes that contain a thiazine ring structure as shown in Figure 1. These dyes are commonly used in various industrial applications, including textile dyeing, paper colouring, and as biological stains. The toxicity of thiazine dyes in water can vary depending on the specific dye and its chemical composition (Handbook of Green and Sustainable Nanotechnology, 2023; Rani and Shanker, 2023; Abilaji et al., 2023). In general, some thiazine dyes may pose environmental and health risks due to their potential toxicity. Many synthetic dyes, including MB dyes, are known to be persistent in the environment and may be resistant to biodegradation. Consequently, they can accumulate in water bodies, leading to potential adverse effects on aquatic ecosystems (Selvaraj et al., 2021; Zosenko et al., 2022). Scheme 2 outlines general



SCHEME 2
Toxicity effect of thiazine dyes in water.

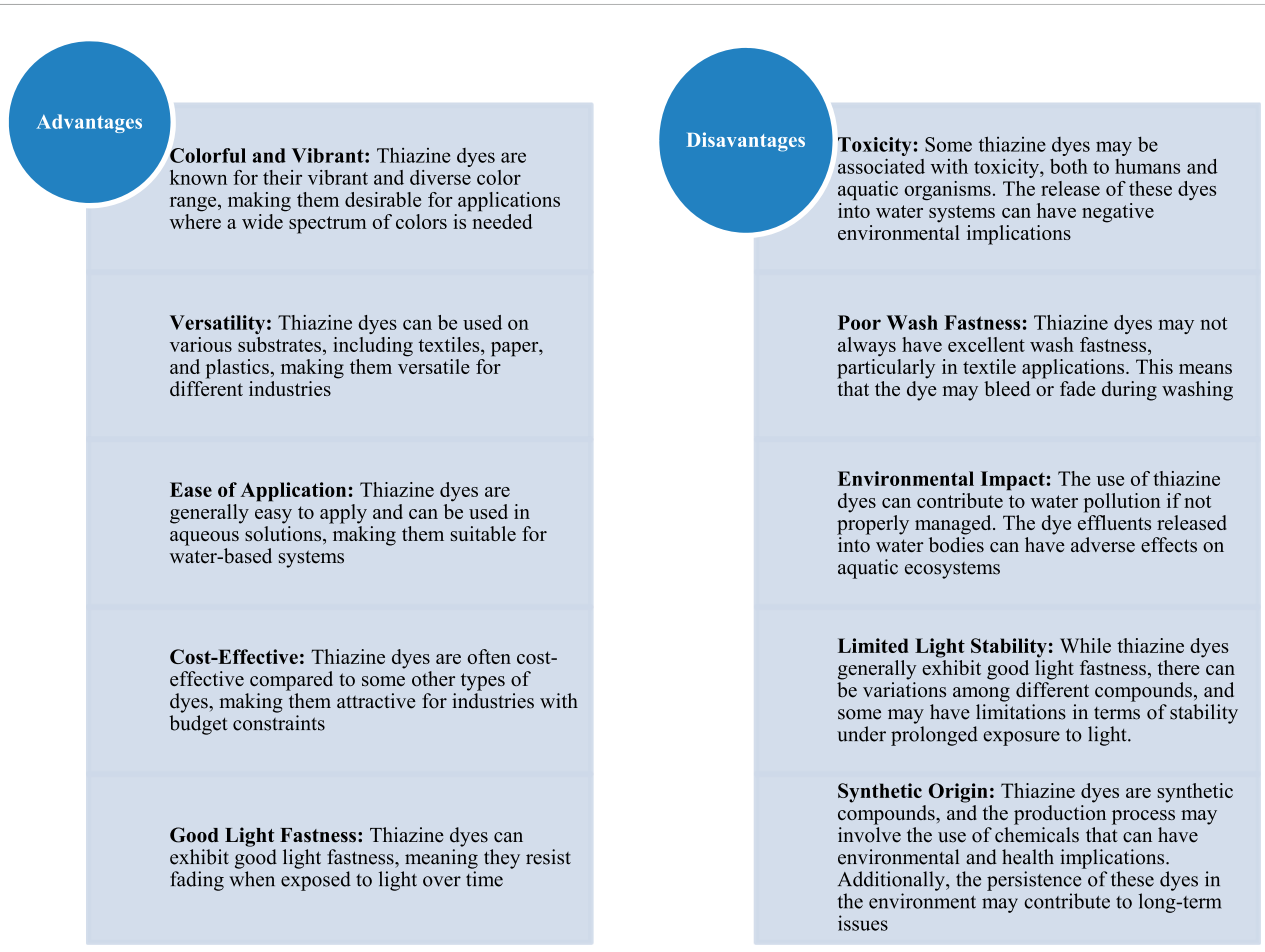
considerations regarding the potential toxic effects of thiazine dyes.

To assess the toxicity of a specific thiazine dye, it is necessary to consider factors such as its chemical structure, concentration in water, and the sensitivity of the organisms present in the aquatic environment. Toxicity studies and risk assessments are typically conducted to evaluate the potential harm of specific chemicals, including dyes, to aquatic organisms and human health (Oladoye et al., 2022; Khan et al., 2023). It is important to note that regulations and guidelines exist to limit the release of certain dyes into water bodies to mitigate potential environmental and health risk.

5.2 Applications of thiazine dyes in water treatment

Thiazine dyes, particularly exemplified by methylene blue, are recognized as versatile organic dyes with well-established applications in various scientific and technological domains. Their significance extends across chemical, biological, and medical applications, making them indispensable in these fields. In the realm of wastewater treatment, thiazine dyes such as methylene blue play a crucial role in addressing environmental concerns (Paul and Suresh Kumar, 2013). Notably, thiazine dyes exhibit unique properties, including solva-tochromism and metachrosis, making them highly sensitive to changes in their surroundings. Additionally, their high singlet oxygen quantum yields contribute to their efficacy in specific applications. In the context of wastewater treatment, these dyes can be strategically modified to create derivatives with enhanced functionality, allowing for the introduction of new substituents at the nitrogen or CH groups (Montalti et al., 2006; Talman and Atun, 2006). As such, thiazine dyes, like many other synthetic dyes, have both advantages and disadvantages in various applications, including their use in water-based systems. Scheme 3 outlines of some potential advantages and disadvantages of thiazine dyes in water.

The majority of dye producers and consumers, especially those in the textile industry, discharge large amounts of wastewater that contains dye in amounts between 0.001 and 0.7% w/v (see Figure 8) (Langhals and Zollinger, 2004). A review of papers on textile industry wastewater treatment for the removal of different dyes revealed that advanced oxidation processes, such as photocatalysis and Fenton reactions, showed the highest colour removal efficiency (GilPavas et al., 2018; Rashid et al., 2021). However, the research did not clearly demonstrate the impact of green technologies on energy consumption, carbon footprint, and waste generation. New technologies need to be developed and evaluated in a sustainable context with real wastewater. The denim textile industry generates



SCHEME 3
Some potential advantages and disadvantages of thiazine dyes in water.

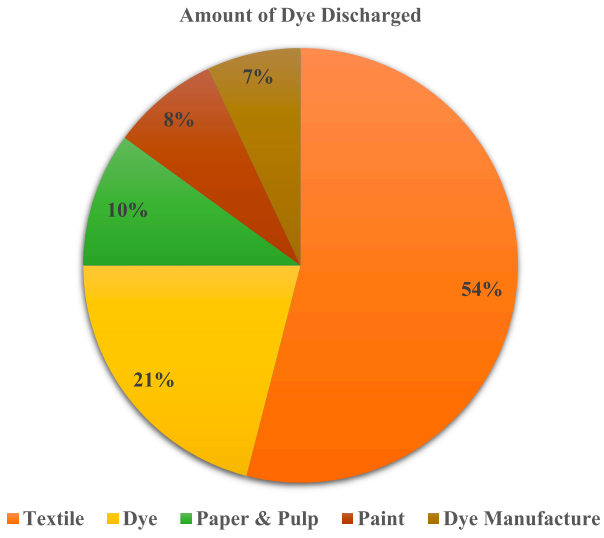


FIGURE 8
Percentage of global dye pollution across industries.

wastewater with persistent pollutants, which can be toxic and carcinogenic. Wastewater treatment is important to reduce risks to aquatic life and public health (GilPavas et al., 2018; Rashid et al., 2021; Kishor et al., 2021).

As shown in Figure 8, the textile dyeing and finishing processes involve the extensive use of dyes, and the wastewater generated during these processes often contains significant amounts of dye residues. The most widely used thiazine dyes i.e., MB is applied in dye silk, cotton, and wood. The wastewater containing dyes is characterized by elevated alkalinity, low biodegradability, total dissolved solids (TDS), chemical oxygen demand (COD), and biochemical oxygen demand (BOD) (Srinivasan and Viraraghavan, 2010). Since dye is colourful, it is simple to detect its presence in water bodies, and it easily blocks sunlight and eventually the water bodies ability to reoxygenate thereby interfering with aquatic life's biological processes. Industrial dye effluent can be colored-free using a variety of techniques. However, due to the wide variety of dyes on the market and the presence of additional chemicals in industrial effluent, many treatment techniques may not be effective when used alone and may need to be combined with other techniques to remove most of the colouring. There are three types of dye wastewater treatment methods viz., chemical, biological, and physical treatments (Crini and Lichtfouse, 2019; Hung et al., 2017; Hung et al., 2020). When not properly treated, this wastewater can be discharged into rivers and other water bodies, causing environmental pollution thiazine dye derivatives, when employed as photosensitizers in PDT processes, offer several advantages. These include high selectivity, resulting in reduced toxicity to healthy tissue, improved cosmetic outcomes, dual functionality during application, a lower risk of infection, absence of organ damage, diminished likelihood of inducing resistance, and minimal side effects such as infertility. Moreover, thiazine photosensitizers in PDT hold promise for combination therapies due to their unique method of action, which makes them resistant to many common chemotherapeutic resistance mechanisms (Callaghan and Senge, 2018; Senge and Radomski, 2013; Spring et al., 2015). Despite these strengths, PDT faces challenges in becoming the primary treatment choice for certain tumours, primarily due to limitations in tissue penetration, light dosage management, and photosensitivity. Nevertheless, PDT remains a clinically useful therapy, and there is a pressing need for innovative approaches to enhance existing therapies. This involves accelerating the development of the third or fourth generation of thiazine photosensitizers to overcome current limitations and potentially revolutionize treatment modalities in relevant fields. Efforts should focus on refining existing methodologies, exploring novel techniques, and fostering collaboration between disciplines to drive transformative advancements in the application of thiazine dyes, such as methylene blue, in wastewater treatment and related areas (Spring et al., 2015).

5.3 Application of thiazine dyes in dye-sensitized solar cells

Thiazine dyes, such as phenothiazine dyes, have limitations that restrict their further optimization for high-efficiency DSSCs (Buene and Almenningen, 2023). However, recent studies have shown the importance of these dyes in achieving higher photovoltaic conversion efficiency (Han et al., 2023). For example, N-phenylphenothiazine dyes with different π-bridges have demonstrated improved J_{SC} and VOC, leading to higher overall efficiency in DSSCs (Hirakawa and Mori, 2021). Additionally, the inclusion of auxiliary acceptors, such as benzothiadiazole, in phenothiazine-based dyes has been shown to broaden their spectral response range and improve device performance (Li et al., 2021). These findings suggest that thiazine dyes can still play a role in sustainable environmental solutions, particularly in the development of highly efficient DSSCs (Wang et al., 2022). However, it is important to consider the potential secondary pollution caused by these dyes and explore alternative options for sustainable environmental solutions. Thiazine dyes have garnered considerable attention for their unique properties, making them promising candidates in various aspects of solar energy conversion. From enhancing light absorption to serving as sensitizers in DSSCs, thiazine dyes play a crucial role in advancing the efficiency and versatility of solar cell technologies (Buene and Almenningen, 2023; Han et al., 2023; Li et al., 2021). Table 3 provides an overview of key applications, showcasing the potential of thiazine dyes across different solar cell architectures and technologies.

As shown on the table, different types of dye sensitizers used in various photovoltaic solar cell devices underscores the diverse strategies employed to harness solar energy for electricity generation. Organic dyes, inorganic dyes, and perovskite materials represent distinct categories of sensitizers, each with unique advantages and challenges (Li et al., 2022; Rani and Shanker, 2023; Takahashi et al., 2023). Organic dyes, characterized by their tunable chemical structures, offer versatility and ease of modification. They have been extensively used in DSSCs, demonstrating good light absorption and electron injection capabilities. However, challenges related to stability and limited absorption in the red and near-infrared regions have prompted exploration into alternative sensitizers (Liu et al., 2023; Li et al., 2021; Lee et al., 2017).

Inorganic dyes, particularly metal complexes like ruthenium-based compounds, exhibit remarkable photostability and extended

TABLE 3 Summary of different types of dye sensitizers used in various photovoltaic solar cell devices

Dye Sensitizer	Description	Study	Photovoltaic performance of DSSCs			
			J_{SC} [$mAcm^{-2}$]	VOC [mV]	FF [%]	Ref
Thiazole-based Co-sensitizer	Thiazine dyes are commonly used as sensitizers in DSSCs. They absorb sunlight and inject electrons into the semiconductor material, initiating the conversion of solar energy into electrical energy.	Innovating dye-sensitized solar cells: Thiazole-based Co-sensitizers for enhanced photovoltaic performance with theoretical insights	19.50	650	64.18	Radwan et al. (2023)
Thieno[3,4-b]pyrazine based dyes	Thiazine dyes serve as effective light-harvesting molecules, expanding the absorption spectrum of solar cells into the visible range. This enhances the overall efficiency of solar energy conversion.	Exploring Different Designs in Thieno[3,4-b]pyrazine-Based Dyes to Enhance Divergent Optical Properties in Dye-Sensitized Solar Cells	14.08	711	74.4	Franchi et al. (2023)
Oxazine and Thiazine	Thiazine dyes can be integrated into various types of photovoltaic devices to enhance light absorption, electron transfer, and overall energy conversion efficiency.	Comparison of dye (oxazine and thiazine) materials as a photosensitizer for use in photogalvanic cells based on molecular interaction with sodium dodecyl sulphate by spectral study	19.0	654	69	Mall et al. (2019)
D-A-π-A Phenothiazine-based	Thiazine dyes are explored for their potential in tandem solar cells, where multiple layers of solar cells with different absorption spectra are stacked to optimize energy absorption and conversion	The application of a novel D–A–π – A phenothiazine-based organic dye with N719 in efficient parallel tandem dye-sensitized solar cells	20.62	720	72.8	Shi et al. (2023)
Phenothiazine-based organic dyes	Thiazine dyes may find applications in organic photovoltaic cells, contributing to the development of lightweight, flexible, and cost-effective solar energy harvesting devices.	The effect of conjugated groups for favorable molecular planarity and efficient suppression of charge recombination simultaneously of phenothiazine-based organic dyes for dye-sensitized solar cells.	10.58	710	58.35	Huang et al. (2022)
Dithizone	Thiazine dyes can be incorporated into hybrid solar cells, combining organic and inorganic materials to achieve synergistic benefits in terms of efficiency and stability.	Improved efficiency and stability of organic-inorganic hybrid perovskite solar cell via dithizone surface passivation effect	22.44	1005	77	Huang et al. (2022)
Phenothiazine dyes	Thiazine dyes play a role in sensitizing semiconductor nanomaterials, enhancing their photoelectrochemical properties and contributing to improved solar cell performance.	Phenothiazine dyes bearing fluorenone unit for dye-sensitized solar cells.	11.46	720	64	Han et al. (2023)
2,2′-bithiophene dye sensitized TiO_2	Incorporation of this dye improved absorption and reduced charge recombination leading to the higher PCE	Design, synthesis, and performance evaluation of TiO2-dye sensitized solar cells using 2,2′-bithiophene-based co-sensitizers.	18.14	676	60.54	Elmorsy et al. (2023)
3,8-substituted phenothiazine dye sensitized TiO_2	This dye lowered the oxidation potential making it more positive hence improved device performance.	Effect of Auxiliary Donors on 3,8-Phenothiazine Dyes for Dye-Sensitized Solar Cells.	10.2	791	76.5	Buene et al. (2019)

absorption spectra (Roy et al., 2023). Their utilization in DSSCs has shown significant efficiency improvements, yet concerns regarding the scarcity and cost of some metal components stimulate ongoing research for more sustainable alternatives. Perovskite materials have emerged as a groundbreaking class of sensitizers, demonstrating rapid advancements in photovoltaic technology (Takahashi et al., 2023). Perovskite solar cells exhibit high efficiency, low-cost fabrication, and a broad absorption spectrum. However, issues related to stability, toxicity, and scalability remain focal points of research efforts.

6 Synthesis and modification of TiO_2-based dye photosensitizers

6.1 TiO_2-based dye photosensitizers

The TiO_2 structure, morphology, and particle size are known to have a significant impact on its optical properties and, consequently, its photoactivity. There are several methods for achieving titanium dioxide photosensitizers, including surface modification using the right species (Moma and Baloyi, 2018). A visible-light-induced

electron or hole injection into the conduction or valence band, respectively, is necessary for the photosensitization process (Hamza et al., 2023; Moma and Baloyi, 2018; Dlamini et al., 2021). The photosensitizer moiety's (surface complex) electrical interaction with the TiO_2 particle determines the process's efficiency. Quantum yields of photoinduced electron transfer processes are also impacted by surface modification of TiO_2 (Hamza et al., 2023; Elmorsy et al., 2023; Monika et al., 2023). Specifically, TiO_2 photosensitization attracts a lot of interest because this material is used as a photoactive material in photovoltaics, optoelectronics, and photocatalysis (Hagfeldt and Grätzel, 2000; Moser et al., 1998; Szaciłowski et al., 2005).

At the surface of TiO_2, several Ti(IV) complexes are generated *in situ*. There may be correlations between the application of TiO_2 phonium and the structures of Ti(IV) complexes, particularly those involving oxygen-ligands (Hug and Bahnemann, 2006). In addition, there are bidentate bridging structures made up of chelating ligand binding two nearby Ti(IV) centres, which is the bidentate chelating structure with the ligand occupying two coordination sites. One oxo ligand must be substituted for other titanium centers coupled with five ligands to create a bidentate chelating complex, although monodentate or bridging complexes can be formed by any of the five surfaces Ti(IV) sites. Meanwhile, the monodentate complexes with coordination between aliphatic alcohols and the surface of titanium dioxide is extensively researched, primarily due to its significant impact on photocatalytic reactions that take place when these molecules are present. The hydroxyl group on the surface of TiO_2 facilitates the physical (molecular) and chemical adsorption of simple aliphatic alcohols, including methanol, ethanol, and 1- and 2-propanol (Kim et al., 1988; Lusvardi et al., 1995). On the other hand, both phenol and 4-chlorophenol bind to the TiO_2 surface with a moderate affinity (Lusvardi et al., 1995; Al-ekabi et al., 1989). The complexes that are produced exhibit poor stability constants. The incapacity of phenol and 4-chlorophenol to form ring-structured surface complexes could be the cause of the observed weak chemisorption.

As summarised in Table 1, bidentate complexes are formed only when the ligand has two donor group photosensitizers or one group with two donor atoms. Physisorption and the monodentate complexation mode are not excluded by the potential for bidentate structures to be formed. Polynuclear complexes results through anchoring of the group photosensitizers, in which different organometallic complexes of transition metals may be attached to the titanium surface centers. In this regards, the carboxyl group photosensitizers can act as anchors leading to the formation of a polynuclear complex with bridging ligands that can coordinate with Ti(IV) and other metal ions. There are many methods used to prepare TiO_2-based material to be used as sensitizers reported in the literature coated on fluorine-doped tin oxide (FTO) glass substrate as thin films. Vinaayak et al. (2022), used a doctor-blade approach to coat TiO_2 nanoparticles on an FTO substrate as a photoanode. Meanwhile, Dhanasekaran and Marimuthu (2023), reported the synthesis of TiO_2 paste from TiO_2 nanopowders, actylacetone, and nitric acid. It was Alaya et al. (2023), who prepared TiO_2 thin films on FTO glass substrates using spray pyrolysis deposition and annealed them at different temperatures for at least 3 hours per thin film. The preparation of these TiO_2 materials was followed by treatment with organic materials such as thiazine dyes, or plant extracts to generate TiO_2-based sensitizers.

6.2 Thiazine and methylene blue-based photosensitizers

Thiazine dyes known as phenothiazines have two benzene rings condensed to the thiazine ring in addition to a central thiazine core. These dyes have lately been explored as photosensitizers due to their biological, photochemical, and photophysical properties (Padnya et al., 2023) with an emphasis on the inactivation of bacterial, viral, and parasite strains (Vara and Ortiz, 2016; Almeida et al., 2020; Shen et al., 2020). Methylene blue and toluidine blue O are two of the most well-known phenothiazines. Methylene blue has been used in clinical settings to treat bacterial infections, including dental conditions, and has shown to be safe, effective, and aesthetically pleasing (Shen et al., 2020; Theodoro et al., 2021). Moreover, methylene blue derivatives, or 3,7-disubstituted dyes of the phenothiazine nucleus, have been produced and functionalized at these sites with a variety of amines for further research into photobiological and optoelectronic uses (Lusvardi et al., 1995). Some compounds derived from phenothiazines are still developed within the purview of their application in cancer PDT, albeit being less prevalent than their antibacterial action. One of the most appealing instances happens when the conjugation of methylene blue with camptothecin *via* an activatable linker containing a disulfide bond that is prone to breakage by GHS (Yang et al., 2022). When administered *in vivo*, no physiological toxicity was observed, indicating safety and biocompatibility.

Thiazine-based photosensitizers hold significant promise for innovative and effective wastewater treatment strategies. These photosensitizers, derived from thiazine dyes like methylene blue, exhibit unique characteristics that can be harnessed for environmental remediation purposes (Vara and Ortiz, 2016; Bindhu et al., 2022). As such, thiazine dyes are well known for their versatility and well-established applications in various scientific fields. When applied as photosensitizers in wastewater treatment processes, these compounds can demonstrate exceptional photodynamic properties (Bindhu et al., 2022). The key attributes that make thiazine and methylene blue-based photosensitizers advantageous in this context include high sensitivity to environmental changes, which thiazine dyes, with their solvatochromism and metachrosis properties, become highly responsive to alterations in the surrounding environment. This sensitivity is crucial for detecting and targeting contaminants in wastewater (Luo et al., 2021; Acar et al., 2015; Bindhu et al., 2022). The high singlet oxygen quantum yields of methylene blue, contribute to their efficacy in inducing photodynamic reactions. This property is particularly beneficial for the degradation of organic pollutants in wastewater.

In this regard, the thiazine-based photosensitizers can also be tailored to selectively target specific contaminants in wastewater (Thandu et al., 2015). This selectivity minimizes the impact on non-target organisms and reduces the overall environmental toxicity of the treatment process. As such, the use of thiazine and methylene blue-based photosensitizers ensures low toxicity in water, which is a

critical factor for sustainable and environmentally friendly wastewater treatment practices (Kenry and Liu, 2022; Thandu et al., 2015). They also offer the potential for combination therapies, allowing for synergistic approaches to enhance wastewater treatment effectiveness. This can involve coupling photodynamic processes with other treatment methods to address a broader range of contaminants. The unique method of action of thiazine photosensitizers makes them less prone to common chemotherapeutic resistance mechanisms (Kenry and Liu, 2022; Barakat et al., 2022; Thandu et al., 2015). This characteristic enhances their reliability and effectiveness in the treatment of wastewater. While thiazine-based photosensitizers present these advantages, it is essential to acknowledge the existing challenges in wastewater treatment, such as the need for optimized dosages, penetration depth, and potential photosensitivity issues (Barakat et al., 2022; Anjum et al., 2019). Ongoing research and development efforts should focus on refining the application methodologies, exploring novel delivery systems, and addressing these challenges to maximize the potential of thiazine-based photosensitizers in wastewater treatment technologies. Through harnessing the unique properties of these compounds, we can advance towards more sustainable and efficient approaches for treating wastewater and safeguarding our environment (Barakat et al., 2022). This led to the conclusion thiazine dye-sensitized TiO_2 could overcome the limits of both camptothecin and methylene blue in terms of their uniqueness.

7 Enhanced photocatalytic applications

Photocatalysis, the process of using a semiconductor material to harness light energy and drive chemical reactions, has gained significant attention in recent years due to its potential to address environmental and energy-related challenges (Jing et al., 2023). Titanium dioxide has emerged as one of the most widely studied photocatalysts, owing to its stability, low cost, and excellent photoactivity in the ultraviolet (UV) region (Magalhães et al., 2017; Yang and Wang, 2018; Lakhera and Neppolian, 2021). The incorporation of MB dyes with TiO_2 for photocatalytic applications has been explored for its ability to enhance light absorption and promote specific chemical reactions (Gonuguntla et al., 2023). However, MB dye remains a health hazard to the environment. Figure 9 demonstrates the efficiency of photocatalytic degradation of organic dyes by AgNP/TiO_2/$Ti_3C_2T_x$ MXene composites under UV and solar light.

The degradation of organic pollutants in water is a crucial aspect of water treatment. Thiazine dyes, which are often used in the textile industry and can be harmful to the environment, can be effectively removed through photocatalysis using TiO_2-based systems. Studies have focused on the degradation of methylene blue, rhodamine B, and other thiazine dyes (Vara and Ortiz, 2016; Acar et al., 2015). Researchers have investigated the optimal conditions for photocatalytic water treatment, including dye concentration, pH, and TiO_2 catalyst loading. The process not only degrades the dyes

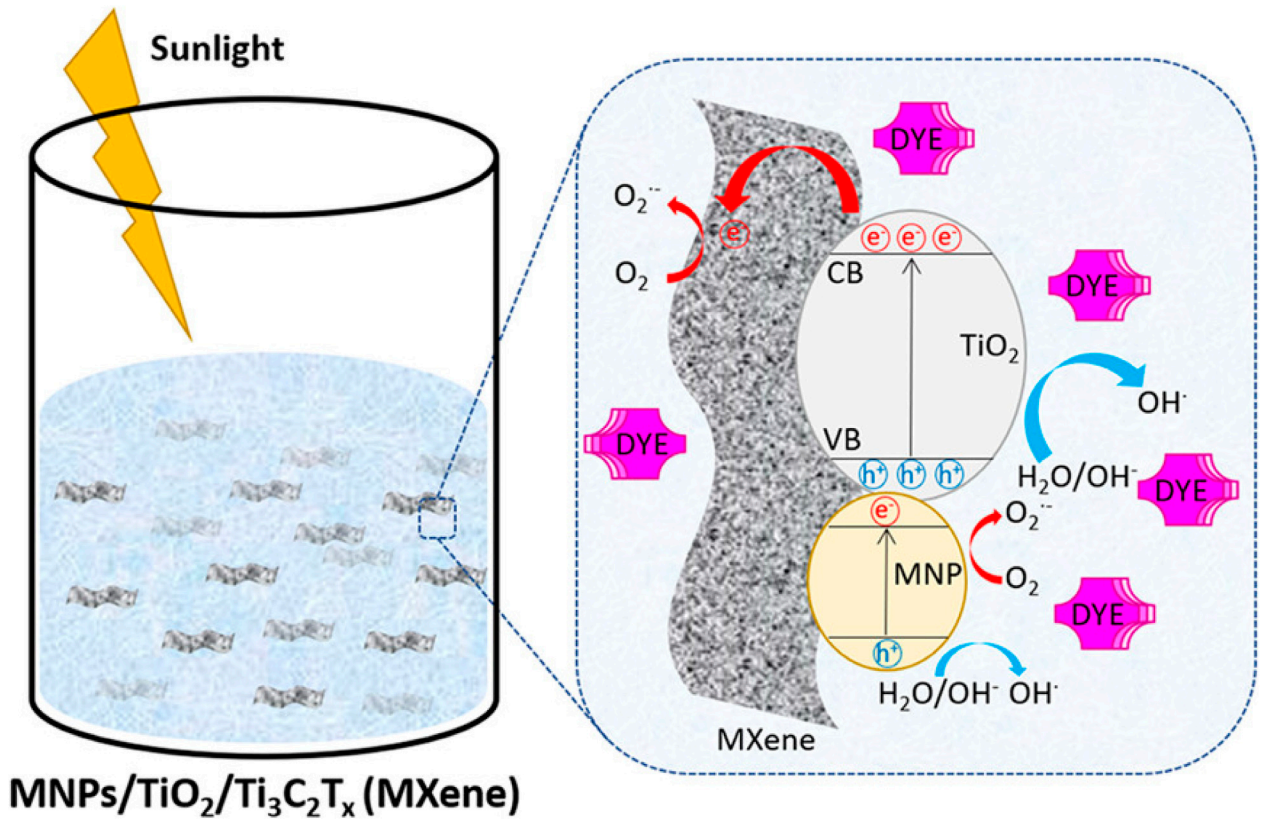


FIGURE 9
Efficient photocatalytic degradation of organic dyes by Silver nanaoparticles/TiO_2/$Ti_3C_2T_x$ MXene composites under UV and visible light (Othman et al., 2021).

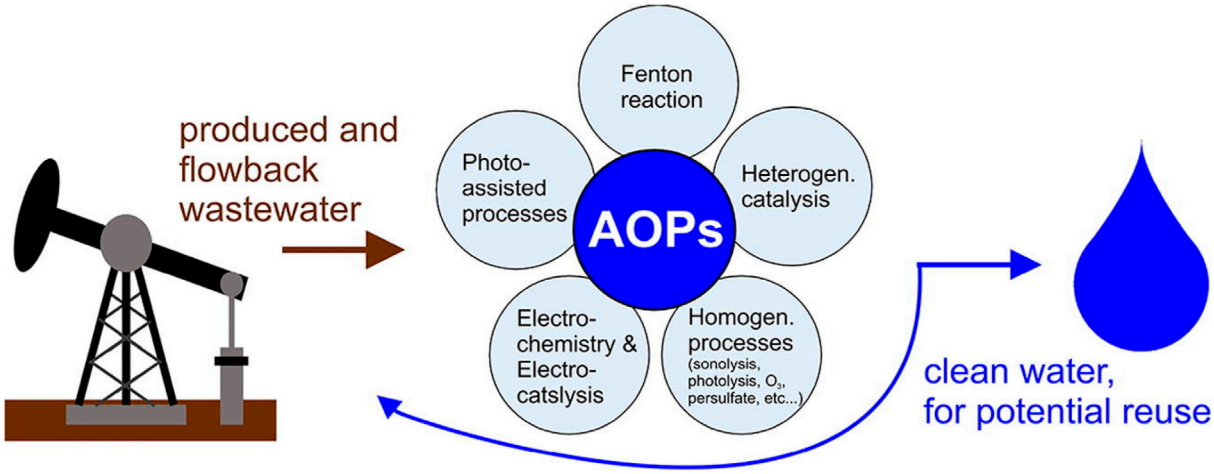


FIGURE 10
Advanced oxidation processes in the removal of organic substances from produced water: Potential, configurations, and research needs (Coha et al., 2021).

but can also lead to the formation of less harmful or non-toxic intermediates.

Beyond thiazine dye removal, TiO_2-thiazine dye systems have been extended to the degradation of other organic pollutants. Barakat et al. (2022) successfully used methylene blue dye as a photosensitizer in the water photo-splitting process, which exhibited enhancement in the hydrogen and oxygen production rates under visible light radiation. As such, the hydrogen and oxygen obtained were in good stoichiometric rates (Barakat et al., 2022). The SiO_2 nanoparticles incorporated into nanostructured TiO_2 was observed to greatly enhance dye photodegradation (Barakat et al., 2022; Senthilkumar et al., 2010). The use of use of methylene blue as a photosensitizer in the form of a methylene blue derivate MB2, which was encapsulated or grafted onto ultrasmall silica nanoparticles for photodynamic therapy applications was reported by Kohle et al. (2020). They found out that singlet oxygen quantum yields improved with particle designs while the encapsulation improved photostability.

Various organic compounds, such as pharmaceuticals, pesticides, and industrial effluents, have been studied in the context of AOP. The synergistic effect of the dye sensitizer with TiO_2 enhances the degradation efficiency of these pollutants under UV or visible light irradiation. Figure 10 demonstrates advanced oxidation processes in the removal of organic substances from produced wastewater: potential, configurations, and research needs

Photocatalytic water splitting is a promising method for hydrogen production, which is a clean and renewable energy source. TiO_2-based photocatalysts, with or without dye sensitizer, have been investigated for their ability to generate hydrogen gas through water splitting (Tentu and Basu, 2017; Villa et al., 2021). The presence of dye sensitizer can extend the absorption range of TiO_2 into the visible region, increasing the overall efficiency of the process. Understanding the mechanisms underlying TiO_2-based dye sensitizer systems is essential for optimizing their performance (Elmorsy et al., 2023; Zani et al., 2021). Studies have employed various techniques, including transient absorption spectroscopy, EPR, and DFT calculations, to gain insights into the charge transfer processes, radical formation, and energy levels of the materials involved (Qian et al., 2019; Bonke et al., 2021).

TiO_2 nanoparticles have been extensively studied for their photocatalytic activity in the degradation of toxic dyes and typical application are summarised on Table 4. As shown on the table, the addition of fluorine and tin dopants to TiO_2 nanoparticles has been shown to enhance their photocatalytic activity (Bindhu et al., 2022). The doped TiO_2 nanoparticles exhibit a reduced crystallite size and an increased band gap, indicating improved photochemical activity (Bindhu et al., 2022; Zioui et al., 2022). The morphologies of TiO_2 nanoparticles also change significantly with the addition of fluorine and tin dopants (Bindhu et al., 2022). These doped TiO_2 nanoparticles have been found to be effective in the degradation of methylene blue dye under both visible and UV light irradiation. Additionally, nanocomposite membranes based on chitosan biopolymer containing TiO_2 nanoparticles have been developed and shown to have high photocatalytic activity in the degradation of tartrazine dye under solar light irradiation (Zioui et al., 2022). Overall, TiO_2 nanoparticles, especially when doped with fluorine and tin, have shown promise in the photocatalytic degradation of thiazine dyes.

Table 4 presents a comprehensive summary of TiO_2-based photocatalytic applications in dye removal, highlighting key studies and outcomes in the realm of environmental remediation. This compilation offers a concise overview of the diverse approaches and methodologies employed in utilizing TiO_2 as a photocatalyst for the degradation and removal of various dyes from aqueous solutions. The studies included cover a spectrum of dyes, showcasing the versatility and effectiveness of TiO_2-based photocatalysis in addressing environmental challenges associated with dye pollutants.

As shown on the table, the ZnO-TiO_2 and ZnO-TiO_2-reduced graphene oxide (ZT-rGO) nanocomposites were synthesized using a pulse laser ablation protocol (Manda et al., 2023). The effect of reduced graphene oxide (rGO) loading on the crystalline nanostructures, thermal stability, and removal of methylene blue dye was investigated by Manda et al. (2023). The ZT-rGO 5 nanocomposite showed the best photocatalytic activity, with a

TABLE 4 Summary of TiO_2 based Photocatalytic application in Dye removal

Photocatalyst Material	Dye Pollutant	Rate Constant (/min)/Period (min)	Photodegradation (%)	Light Source	Eg (eV)	Ref
Sn–F/TiO_2 NPs	MB	0.0345 and 0.987	91 and 94.4	UV and Visible Light	~3.28	Bindhu et al. (2022)
TiO_2-Chitosan	Tartrazine dye	~	83	Solar Light	~	Zioui et al. (2022)
ZnO-TiO_2-rGO	MB	0.149	98.5	UV	~2.53	Manda et al. (2023)
TiO_2/$CaIn_2S_4$@rGO	MB and CR	0.027	99	UV	~	Chaudhari et al. (2022)
TiO_2/C	MB	~	100	Simulated Sun Light	~2.7	jie Song et al. (2023)
Au-TiO_2	MB	0.1570	~	UV	~	Khalil et al. (2019)
TiO_2 nanostructure	RB	~0.120 and 0.107	93.8	UV	~3.0	Kiwaan et al. (2020)
N719 Dye-sensitized TiO_2	MB	25 min	99	UV-Visible	3.2	Herath et al. (2020)
chlorophyll Dye-sensitized TiO_2	MB	120 min	85	Visible light	2.83	Krishnan and Shriwastav (2021)
Chlorophyll/TiO_2:W composite	RB	120 min	94 - 100	UV-Visible	~	Valadez-Renteria et al. (2022)
mangosteen dye-sensitized-TiO_2	MB	120 min	78	Visible light	2.95	Ghosh et al. (2020)
Eosin Y (Ey) Dye-sensitized TiO_2	Acetaminophen	180 min	71	UV-Visible	Not reported	Diaz-Angulo et al. (2019)
Quinazoline-derivative dye-sensitized-TiO_2	RB	0.0226 and 0.0146	98% under UV 83% under Visible	UV -Visible	2.6	Hamza et al. (2023)

NPs, nanoparticles; rGO, reduced graphene oxide; CR, Congo Red; MB, Methylene Blue; RB=Rhodamine B.

preferential rate constant of 0.149 min^{-1} and 98.5% methylene blue removal within 30 minutes. The rGO component in the nanocomposites acts as an electron trap, enhancing the formation of holes and contributing to the photocatalytic process (Manda et al., 2023). Chaudhari et al. (2022) conducted a novel $TiO_2CaIn_2S_4$rGO composites (rGO-C_1 to rGO-C_3) synthesis for rapid degradation of organic dye. In their study, the rGO-C_2 exhibited significant photocatalytic degradation activity for MB CR within 15-30 min. Analysis by the LC-MS technique discovered the degradation pathway of both dyes. As such, the rGO-C_2 catalyst showed excellent degradation activity for real wastewater from the textile industry and landfill leachate (Chaudhari et al., 2022). A study by Song et al. (2023) reported that the direct band gap of the titanium dioxide carbon (TiO_2C-550) composite was 2.7 eV, which lead to the improved photodegradation performance of MB under visible light irradiation. As such, the degradation ratio of MB aqueous solution reached nearly 100% within 30 minutes in the presence of TiO_2C-550 composites, and the efficiency was maintained at about 95% after 5 cycles (jie Song et al., 2023). The Au-TiO_2 nanospindles were found to be the most efficient catalyst for photocatalytic degradation of MB, with a pseudo-first order reaction rate of 0.1570 min^{-1} by Khalil et al. (2019). They showed that TiO_2 nanospindles exhibited superior photocatalytic performance compared to TiO_2 nanocubes, which was primarily due to the exposure of the (001) crystal facet (Khalil et al., 2019).

It is clear that researchers have explored different approaches to modify TiO_2 and thiazine dyes to enhance their photocatalytic properties. Other modifications include doping TiO_2 with various elements, such as nitrogen or metal ions, and designing new thiazine dyes with tailored properties. Such modifications aim to extend the absorption range, improve charge separation and transportation, and increase the overall efficiency of the photocatalytic systems (Chakhtouna et al., 2021; Humayun et al., 2018). The exploration of photocatalytic processes using TiO_2-based dye sensitizer systems has shown great promise in addressing various environmental and energy-related challenges. The field continues to evolve, with researchers focusing on optimizing materials and conditions, gaining a deeper understanding of the mechanisms involved, and expanding the range of applications (AlSalka et al., 2023; Anucha et al., 2022; Zani et al., 2021; Tentu and Basu, 2017). Further research is needed to bridge the gap between laboratory-scale experiments and practical, large-scale implementations for water treatment, pollutant degradation, and hydrogen production. Comparison of the performance of thiazine dye-sensitized TiO_2 with other sensitization strategies still require extensive exploration.

8 Future directions and prospects TiO_2-based thiazine dye photosensitizers

This comprehensive review meticulously delves into the current challenges and future prospects of TiO_2-based thiazine dye sensitizers, aiming to significantly enhance their performance and broaden their applicability. Overcoming the formidable challenge of achieving optimal photocatalytic efficiency in TiO_2-based thiazine dye systems necessitates a nuanced understanding of the intricate dynamics involved in charge carrier generation, separation, transportation, and the reduction of electron-hole recombination. Innovative strategies, including fine-

tuning the chemical composition of thiazine dyes, optimizing TiO_2 morphology, and integrating co-catalysts, offer avenues for addressing existing drawbacks. Elucidating the detailed mechanisms and dynamics of TiO_2-based thiazine dye photosensitization is crucial for successful optimization, although the complexity of these processes poses a significant challenge.

The stability and longevity of TiO_2-based thiazine dye systems emerge as critical factors for sustained photocatalytic activity. Effectively addressing challenges such as dye desorption, catalyst radiation, and the loss of active sites over time requires exploration into surface modification techniques and material engineering. This involves the development of new materials or coatings to mitigate issues related to catalyst degradation and dye desorption. Despite the efficacy of thiazine dyes in photocatalysis, concerns regarding potential toxicity necessitate rigorous toxicity studies and risk assessments. Concurrently, researchers actively explore alternative dye structures or modifications to mitigate environmental and health risks associated with these dyes.

The scalability of TiO_2-based thiazine dye photosensitizers for practical applications introduces challenges related to cost, efficiency, and feasibility. Therefore, collaboration between researchers and industry partners is essential to work towards scalable synthesis methods, cost-effective production, and exploring viable applications, ensuring the practical implementation of TiO_2-based thiazine dye systems. Addressing these multifaceted challenges demands a multidisciplinary approach encompassing materials science, chemistry, and engineering. Ongoing research efforts are dedicated to overcoming these challenges, propelling TiO_2-based thiazine dye systems towards their full potential for sustainable and effective environmental applications. This interdisciplinary journey holds the promise of delivering innovative solutions and ushering in a new era of environmental technologies.

9 Conclusion

TiO_2-based dye photosensitizers have shown potential to enhance the performance of TiO_2-based photocatalysis, particularly in applications such as water splitting to produce hydrogen and pollutant degradation in wastewater. The presence of thiazine dye-sensitizer extends the absorption range of TiO_2 into the visible region, increasing overall efficiency as a photocatalyst or a light adsorbing material in photovoltaic cells. Various modifications, including doping TiO_2 with elements like nitrogen or metal ions, and designing tailored thiazine dyes, aim to extend adsorption range, which inherently leads to improved charge carrier generation, separation, and transportation, and increase overall efficiency of the photocatalytic systems. Mechanistic insights into charge transfer processes, radical formation, and energy levels of the materials involved have been gained through techniques such as transient absorption spectroscopy, electron paramagnetic resonance, and density functional theory calculations. The exploration of TiO_2-based dye sensitizer systems continues to evolve, with researchers focusing on optimizing materials and conditions, expanding the range of applications, and bridging the gap between laboratory-scale experiments and large-scale implementations. In this regards, the use of TiO_2-based photosensitizers shows promise in enhancing the photocatalytic removal of thiazine dyes, such as methylene blue, from wastewater, thereby addressing environmental remediation and energy conversion needs. Thiazine dyes, when coupled with TiO_2, act as effective photosensitizers, promoting electron transfer and generating reactive oxygen species that initiate chemical reactions, making them valuable in applications like wastewater treatment and solar energy conversion. However, it is important to acknowledge the potential drawbacks of thiazine dyes, including toxicity and non-biodegradability. Non-radiative energy transfer processes, such as Förster resonance energy transfer and dexter energy transfer, play a significant role in fluorescence microscopy, molecular biology, and energy transfer-based sensors. Electron Paramagnetic Resonance spectroscopy provides exceptional sensitivity and specificity in characterizing paramagnetic centers formed upon irradiation of photocatalysts like TiO_2, aiding in understanding electron-hole recombination and the nature of trapped charge carriers. Efforts should focus on refining existing methodologies, exploring novel techniques, and fostering collaboration between disciplines to enhance TiO_2-based thiazine photosensitizers and revolutionize treatments modalities in wastewater and related areas. Therefore, TiO_2-based thiazine dye photosensitizers hold promise for improving the efficiency and expanding the applications of TiO_2-based photocatalysis, with ongoing research aimed at further optimization and practical implementations.

NB: This review aims to provide a comprehensive understanding of TiO_2-based dye photosensitizers and their role in enhancing the photocatalytic activity of TiO_2, with a focus on applications in environmental remediation and renewable energy generation. As such, it will be valuable for researchers, chemists, and engineers interested in harnessing visible light for efficient and sustainable photocatalytic processes.

Author contributions

NC: Conceptualization, Formal Analysis, Funding acquisition, Investigation, Project administration, Resources, Writing–original draft, Writing–review & editing. RM: Conceptualization, Writing–review & editing. SN: Conceptualization, Writing–review & editing. MR: Funding acquisition, Project administration, Supervision, Writing–review & editing.

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