Water Science & Technology

Water Science & Technology Vol 88 No 6, 1495 doi: 10.2166/wst.2023.288

A review of the photocatalytic degradation of organic pollutants in water by modified TiO_2

Xueqi Li [a,*], Hongyan Wei[a], Tiehong Song[a], Hai Lu[b] and Xiaoyan Wang[b]

[a] Changchun University of Architecture and Civil Engineering, Changchun 130000, China
[b] Key Laboratory of Songliao Aquatic Environment, Ministry of Education, Jilin Jianzhu University, Changchun City, Jilin Province, China
*Corresponding author. E-mail: lixueqi1027@163.com

XL, 0009-0009-5552-8885

ABSTRACT

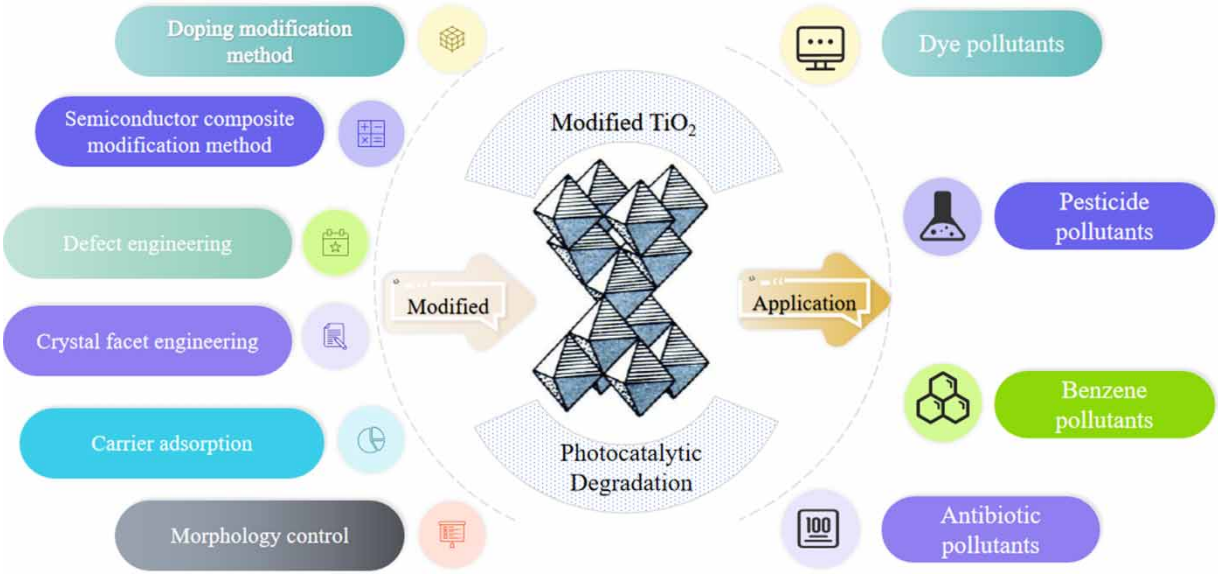
Organic pollutants in water bodies pose a serious environmental problem, and photocatalytic technology is an efficient and environmentally friendly water treatment method. Titanium dioxide (TiO_2) is a widely used photocatalyst, but it suffers from some drawbacks such as a narrow light response range, fast charge recombination, and low photocatalytic activity. To improve the photocatalytic performance of TiO_2, this article reviews the preparation methods, performance evaluation, and applications of modified TiO_2 photocatalysts. Firstly, the article introduces the effects of doping modification, semiconductor composite modification, and other modification methods on the structure and properties of TiO_2 photocatalysts, as well as the common characterization techniques and activity test methods of photocatalysts. Secondly, the article discusses the effects and mechanisms of modified TiO_2 photocatalysts on degrading dye, pesticide, and other organic pollutants in water bodies, as well as the influencing factors. Finally, the article summarizes the main achievements and advantages of modified TiO_2 photocatalysts in degrading organic pollutants in water bodies, points out the existing problems and challenges, and prospects for the development direction and future of this field.

Key words: degradation, modification, organic pollutants, photocatalysis, titanium dioxide

HIGHLIGHTS

- Various techniques enhance titanium dioxide (TiO_2) properties.
- The study of the modified TiO_2 photocatalytic mechanism.
- Modified TiO_2 excels in degrading organic pollutants.
- In practical water treatment, modified TiO_2 offers promising results and simultaneous challenges.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Water is a precious resource on Earth, which is crucial for maintaining the ecological balance and ensuring the sustainable development of human society (Gavrilescu 2021). However, rapid industrialization, urbanization, and agricultural growth have led to an increasingly severe problem of organic pollutant contamination in water bodies, becoming one of the significant challenges in global environmental protection (Mushtaq *et al.* 2020). These organic pollutants in water primarily originate from industrial wastewater, agricultural runoff, urban sewage, and various human activities (Singh *et al.* 2020). Not only are these pollutants highly stable and difficult to degrade, but they may also pose threats to water quality and the ecosystem due to their potential toxicity, carcinogenicity, and mutagenicity (Ismail *et al.* 2019).

Therefore, there is an urgent need to explore efficient, economical, and environmentally friendly methods to remediate organic pollutants in water bodies. In recent years, photocatalytic technology has garnered considerable attention as an environmentally friendly approach to pollutant degradation (Subhiksha *et al.* 2022). This technology harnesses photocatalysts to generate highly active oxygen radicals, such as hydroxyl radicals ($^{\bullet}OH$) and superoxide radicals ($^{\bullet}O_2^-$), under light irradiation (Acharya & Parida 2020). These radicals can oxidize and decompose organic pollutants in water, transforming them into harmless small molecules like carbon dioxide and water (Jiang *et al.* 2021). Among various photocatalysts, titanium dioxide (TiO_2) has been extensively studied due to its advantages of low toxicity, high stability, affordability, and excellent chemical stability (Zhang *et al.* 2019; Turkten & Bekbolet 2020; Li *et al.* 2021a, 2021b).

However, TiO_2 also suffers from some limitations, such as a narrow light absorption range, rapid electron-hole recombination rate, and low catalytic activity, which hinder the practical application of TiO_2 photocatalysis (Jeon *et al.* 2020). To address these issues, researchers have focused on modifying TiO_2 photocatalysts to enhance their photocatalytic performance (Arora *et al.* 2022). Modified TiO_2 photocatalysts, achieved through the introduction of dopants, loading agents, or composites, can modulate TiO_2's band structure, electronic transport properties, and surface characteristics, thereby effectively improving photocatalytic activity and selectivity (Chen *et al.* 2020).

It is worth noting that despite the existence of numerous review articles on TiO_2 as a photocatalyst, this study stands out with its clear thematic focus and distinct motivation. The paper thoroughly discusses the performance of modified TiO_2 photocatalysts, explores the underlying mechanisms of various modification methods, and discusses their efficiency in degrading organic pollutants in water. Additionally, special attention is given to the application of modified TiO_2 photocatalysts in degrading diverse types of organic pollutants, highlighting their crucial value and promising prospects in treating organic water pollution.

Consequently, this paper aims to delve into the application of modified TiO_2 photocatalysts in the degradation of organic pollutants in water bodies, exploring their potential in addressing water environmental issues. Through this research, we anticipate providing new insights and methods for treating organic pollutants in water bodies and promoting the widespread adoption and application of photocatalytic technology in practical scenarios.

2. MATERIALS AND METHODS

2.1. Preparation methods of modified TiO_2 photocatalysts:

2.1.1. Doping modification method

Doping modification is a technique that introduces different impurity elements into the TiO_2 lattice. It has several advantages for enhancing the photocatalytic performance of TiO_2 (Cao *et al.* 2021). First, it can promote the formation of the anatase phase, which has higher activity than the rutile phase (Anitha & Khadar 2020). Second, it can reduce the grain size and increase the specific surface area and light absorption capacity of TiO_2 (Zhang *et al.* 2020). Third, it can adjust the band gap and conduction band (CB) position of TiO_2, thus extending its visible light response range and photo-generated carrier separation efficiency (Yao *et al.* 2023). Fourth, it can increase the number of surface hydroxyl groups and oxygen vacancies of TiO_2, thus improving its adsorption capacity and redox ability for organic pollutants (Ansari *et al.* 2016; Liu *et al.* 2016). The doping elements can be classified into two types: metal elements and non-metal elements. Metal element doping can create new energy levels within the band gap of TiO_2, enabling it to absorb visible light. For instance, TiO_2 doped with metal elements, such as iron, cobalt, nickel, and copper, can exhibit different colors and degrade organic pollutants more effectively (Basavarajappa *et al.* 2020). Non-metal element doping can alter the electron affinity and ionic radius of TiO_2, affecting its charge transfer and recombination process. For example, TiO_2 doped with non-metal elements, such as nitrogen, sulfur, and carbon, can increase the electron density of the CB and suppress the hole recombination, thus enhancing its photocatalytic activity (Sedrati *et al.* 2014; Zhang *et al.* 2021a, 2021b, 2021c). Bagwasi *et al.* (2013) conducted research on the photocatalytic degradation mechanism of 2,4-dichlorophenol (2,4-DCP) using 10% bismuth-modified nitrogen-doped TiO_2 (Bi/N-TiO_2) under visible light irradiation. The proposed degradation mechanism is illustrated in Figure 1. The research revealed that substitutional nitrogen in the nitrogen-doped TiO_2 (N-TiO_2) creates a new state just above the valence band (VB) of TiO_2, resulting in a narrower band gap that enables visible light absorption. During visible light irradiation, four possible transition routes are proposed for the degradation of 2,4-DCP: excited electrons from the nitrogen impurity band are transferred to the CB of TiO_2 and possibly further transferred into the CB of $Bi_{20}TiO_{32}$ particles through a heterojunction formed between N-TiO_2 and $Bi_{20}TiO_{32}$. Electrons formed from the nitrogen impurity band are captured by oxygen molecules, leading to the generation of superoxide radicals ($^{\bullet}O_2^-$). Superoxide radicals react with electrons and protons, forming hydrogen peroxide (H_2O_2), and hydrogen peroxide reacts with superoxide radicals, resulting in the formation of hydroxyl radicals

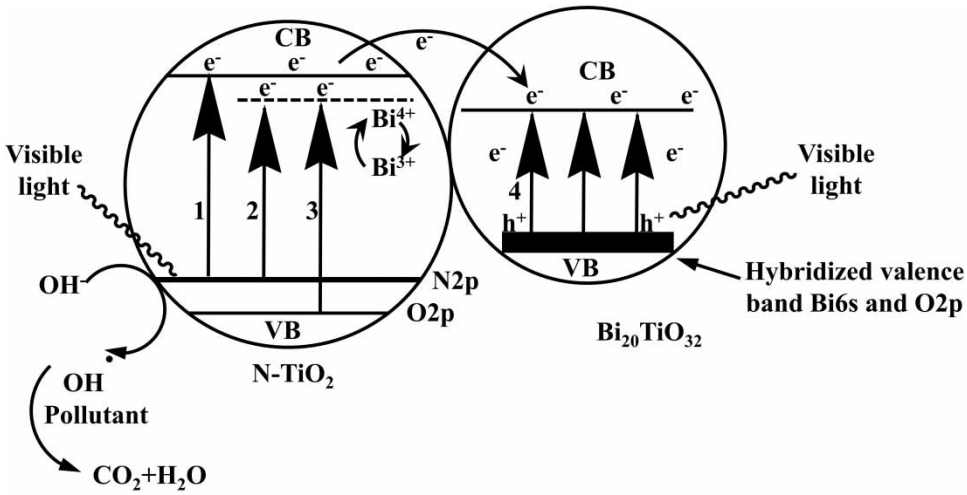


Figure 1 | Mechanism for the degradation of 2,4-DCP by 10% Bi/N-TiO_2 under visible light irradiation (Bagwasi *et al.* 2013).

(OH˙), hydroxide ions (OH^-), and molecular oxygen (O_2) through a series of reactions. The visible light absorption by Bi/N-TiO_2 and the effective charge carrier separation facilitated by bismuth species play a significant role in enhancing the photocatalytic activity of Bi/N-TiO_2 for the degradation of 2,4-DCP. Bayan *et al.* (2020) conducted a study and found that co-doping TiO_2 with zinc and fluorine ions induces the formation of oxygen vacancies on the catalyst surface. The presence of these vacancies enhances the generation of hydroxyl radicals (OH^-) on the nanoparticle surface, which play a crucial role in the photocatalytic process. Additionally, zinc doping influences the formation of active species. Zinc ions (Zn^{2+}) can trap electrons or holes, disrupting their stable configuration. Trapped electrons can react with oxygen molecules to produce superoxide radicals ($^{\bullet}O_2^-$), while trapped holes can react with hydroxyl anions to form hydroxyl radicals (OH^-). In the photocatalytic process, the model pollutant used is the organic azo-dye methylene blue (MB). The cationic functional groups of MB molecules initially adsorb onto the catalyst nanoparticle surface. Subsequently, the radical decomposition of MB takes place, leading to the opening of the central aromatic ring and the formation of intermediate degradation products. Finally, the photocatalytic decomposition culminates in the production of inorganic molecules such as CO_2, SO_4^{2-}, NH_4^+, and NO_3^-. These reactions occur under both UV and visible light irradiation.

2.1.2. Semiconductor composite modification method

One way to modify the semiconductor composite is to combine TiO_2 with other semiconductor materials such as ZnO, CdS, and Bi_2O_3 (Muangmora *et al.* 2021; Stojadinović *et al.* 2022). This creates a composite structure with band gap matching and heterojunction structure construction, which enhances its visible light response capacity and photocatalytic activity (Gao *et al.* 2022). The co-precipitation method, the hydrothermal method, and the mechanical ball milling method are some of the methods that can realize the semiconductor composite modification. The composite structure can have different forms, such as 0D–0D (quantum dot–quantum dot), 1D–1D (nanowire–nanowire), and 2D–2D (nanosheet–nanosheet) (Chakraborty & Pandey 2023). The main mechanism of the action of the semiconductor composite modification is to promote the effective separation and migration of electron-hole pairs through the heterojunctions, inhibit their recombination, and expand their light absorption range and active sites. Zhang *et al.* (2021a, 2021b, 2021c) prepared a carbon quantum dots/layered mesoporous TiO_2 (CQDs/LM-TiO_2) composite material using an inorganic precipitation–gelation method. The CQDs were synthesized using citric acid as a carbon source via a one-step hydrothermal method, while the layered mesoporous TiO_2 was prepared using titanium sulfate as the titanium source, ammonia as the precipitating agent, and cetyltrimethylammonium bromide (CTAB) as the template agent through an inorganic precipitation–gelation method. Under visible light or ultraviolet light irradiation, the CQDs/LM-TiO_2 composite material generates photo-induced electron-hole pairs. Photo-generated electrons transfer from the CB of LM-TiO_2 to the lowest unoccupied molecular orbital (LUMO) energy level of CQDs, forming a CQDs/LM-TiO_2 heterojunction, effectively suppressing electron-hole recombination. Photo-generated holes capture surface OH^- or H_2O molecules on LM-TiO_2's VB, producing highly oxidative hydroxyl radicals (˙OH), which participate in the oxidation degradation of organic pollutants. Photo-generated electrons adsorb surface O_2 molecules on CQDs, generating superoxide radicals ($^{\bullet}O_2^-$), which further convert to peroxyl radicals (˙H_2) and hydroxyl radicals (˙OH), contributing to the oxidation degradation of organic pollutants. Organic pollutants are oxidatively degraded into inorganic small molecules, such as CO_2 and H_2O, achieving water purification. The study demonstrates that 0.2 wt% CQDs/LM-TiO_2 composite material exhibits the highest photocatalytic activity, achieving a degradation rate of 91.04% for methyl orange within 24 min, which is significantly higher than pure TiO_2 and LM-TiO_2. This enhancement is attributed to CQDs' ability to enhance LM-TiO_2's absorption in the visible light region, improve the separation efficiency of photo-generated charge carriers, and facilitate charge transfer at the heterojunction interface. Liu *et al.* (2019) conducted a study on the synthesis and characterization of Ag_2O nanoparticle-decorated TiO_2 nanofibers to enhance the photocatalytic decomposition of Rhodamine B (RhB) under visible light irradiation. The research findings indicate that the band alignment of the Ag_2O/TiO_2 composite at the heterojunction interfaces is responsible for the improved photocatalytic activity. Before Ag_2O comes into contact with TiO_2, the Fermi level of n-type TiO_2 is slightly below the CB of TiO_2, whereas the Fermi level of p-type Ag_2O is slightly higher than the VB of Ag_2O. When n-type TiO_2 comes into contact with p-type Ag_2O, their Fermi levels align together, forming a continuous new Fermi level. This alignment creates a p–n heterojunction at the interface, leading to a new band structure in the interface region. The different positions of the CB and the VB relative to the Fermi level in Ag_2O and TiO_2 cause electrons to the flow from Ag_2O to TiO_2 along the CB, while holes flow in the opposite direction from TiO_2 to Ag_2O along the VB. The realignment of the energy bands also generates a built-in electric field at the interface, directing from Ag_2O to TiO_2. Under visible light irradiation, Ag^+ in Ag_2O is partially reduced to AgO by photo-induced

electrons, resulting in the formation of metallic Ag on the surface of both Ag_2O and TiO_2. This metallic Ag acts as an electron pool, facilitating the transfer of photoexcited electrons from the CB of p-type Ag_2O to the CB of n-type TiO_2. At the same time, the photo-generated holes are transferred from the VB of TiO_2 to the VB of Ag_2O. The presence of the built-in electric field further enhances the transfer and separation of charges. Electrons react with surface-adsorbed to produce superoxide radicals ($^{\bullet}O_2^-$), while the holes exhibit strong oxidizing ability, directly oxidizing and decomposing RhB. Overall, the p–n heterojunction enhances charge transfer and separation, leading to increased photocatalytic activity. This phenomenon highlights the significance of band alignment in Ag_2O/TiO_2 composites, providing insights into the design and optimization of advanced photocatalytic materials. Figure 2 illustrates the photocatalytic mechanism of p-Ag_2O/n-TiO_2 nanofibers.

2.1.3. Other modification methods

Besides the two methods mentioned above, other ways to modify TiO_2 include defect engineering, crystal facet engineering, carrier adsorption, and morphology control (Wang *et al.* 2023). Defect engineering alters the electronic structure and surface activity of TiO_2 by introducing or adjusting lattice defects such as vacancies, interstitial atoms, or dislocations (Dong *et al.* 2018). Crystal facet engineering modifies the shape and lattice distortion of TiO_2 by selecting different phases or facets, which affect its photocatalytic activity (Liu *et al.* 2014). Carrier adsorption enhances the photocatalytic efficiency of TiO_2 by compositing or loading it with other materials such as graphene, carbon nanotubes (CNTs), and metal oxides to form heterojunctions or increase the specific surface area (Anucha *et al.* 2022). Morphology control improves its light absorption and carrier transport characteristics by controlling the morphology parameters such as particle size, shape, and porosity of TiO_2 (Niu *et al.* 2018).

For ease of readability, a concise summary of other methods for modifying TiO_2 is provided in Table 1.

2.2. Performance evaluation methods of photocatalysts

Modified TiO_2 photocatalysts can be prepared by various methods, but their performance requires evaluation and analysis. Some of the common characterization methods for photocatalysts are X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis). These methods can provide information on the phase, morphology, composition, and band structure of photocatalysts. Some of the common photocatalytic activity test methods are the degradation of organic dyes, water splitting for hydrogen production, and photocatalytic reduction of carbon dioxide. These methods can indicate the efficiency and stability of photocatalysts under different reaction conditions. Some of the common photocatalytic activity evaluation indicators are reaction rate

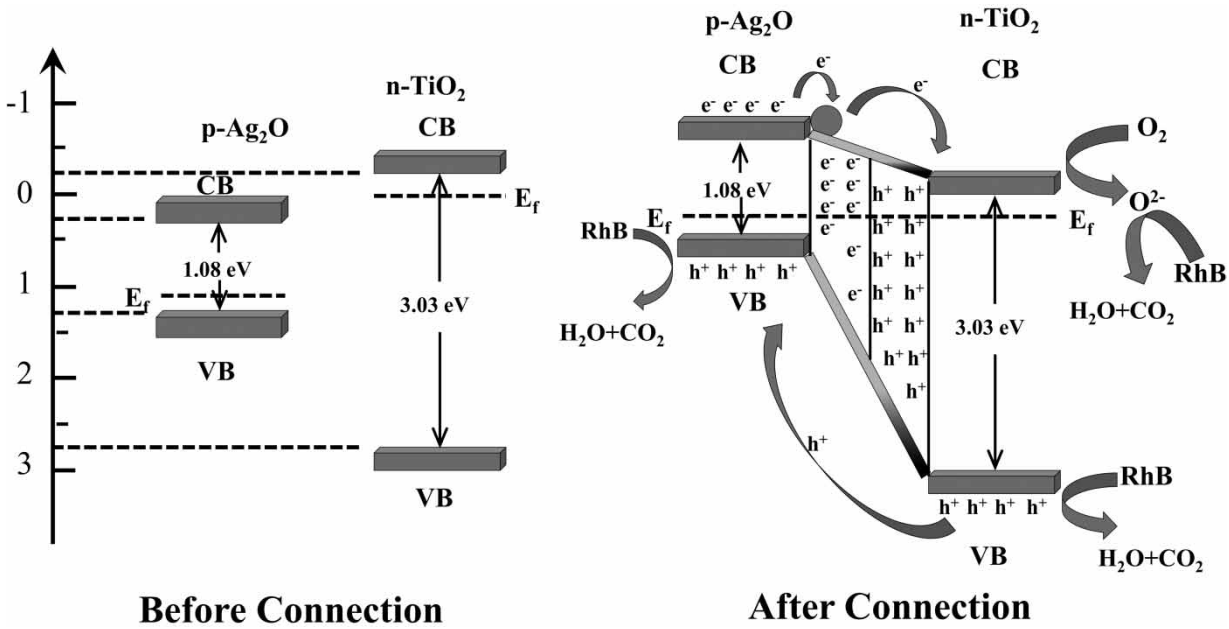


Figure 2 | Proposed photocatalytic mechanism of p-Ag_2O/n-TiO_2 nanofibers (Liu *et al.* 2019).

Table 1 | Other modification methods

Process types	Mechanization	Data sources
Defect engineering	Defect engineering in TiO_2 involves using argon ion beam irradiation to create oxygen vacancies. These vacancies, formed by converting Ti^{4+} ions to Ti^{3+} and Ti^{2+} ions, enhance photocatalytic activity by reducing charge recombination and modifying surface properties and electronic states.	Qahtan *et al.* (2023)
	TiO_2 has defects like oxygen vacancies, Ti^{3+} defects, and grain boundaries. Oxygen vacancies trap electrons, reduce recombination, and improve charge separation. Ti^{3+} defects enhance visible light absorption due to their smaller bandgap than TiO_2's Ti^{4+} states.	Li *et al.* (2022)
Crystal facet engineering	Researchers have enhanced TiO_2's photocatalytic performance by adjusting its crystal facets. Notably, the (101) surface of anatase TiO_2 shows better activity than other facets due to its lower Schottky barrier height that aids efficient electron transfer. This approach also benefits TiO_2 combined with Cr_2O_3, significantly raising CO_2 conversion efficiency.	Fawzi *et al.* (2022)
Carrier adsorption	TiO_2–ZnO/rGO materials have been modified using the hydrophobic compound hexamethyldisilane (HDMS) to enhance their properties. This modification increases the water contact angle to 103.6° by introducing aliphatic carbon groups. HDMS also prevents fouling and water absorption on the material's surface, leading to improved photocatalytic performance. These hydrophobic changes maintain catalytic activity by reducing unwanted water interactions, and significantly enhancing photocatalytic efficiency.	Fadillah *et al.* (2022)
Morphology control	Morphology control in photocatalytic materials hinges on particle size, quantum effects, and carrier migration. Smaller sizes amplify surface area, reactivity, and migration, but proximity to the electron's mean free path can heighten recombination. Nanomaterial morphology, structure, and surface properties also affect carrier migration, necessitating precise concentration or potential gradients. Advances in morphology-controlled synthesis show a link between morphology and photocatalytic traits. Diverse nanostructures, including 0D quantum dots, 1D rods, 2D sheets, and 3D spheres, have been investigated.	Liu *et al.* (2020)

constant, quantum efficiency, and conversion rate. These indicators can quantitatively compare the merits and demerits of different photocatalysts (Cheng *et al.* 2016).

3. RESULTS

3.1. The application of modified TiO_2 photocatalysts in the degradation of organic pollutants in water

3.1.1. Dye pollutants

Dye pollutants are a common type of organic pollutants in aquatic ecosystems. They have high chroma, strong stability, and low biodegradability, which pose serious threats to the water quality (Ma *et al.* 2021). Modified TiO_2 photocatalysts are a novel class of eco-friendly catalysts. They can utilize visible light or ultraviolet light to generate electron-hole pairs, which produce powerful oxidative species such as hydroxyl radicals and superoxide radicals. These species can oxidize and degrade the organic pollutants in water, achieving water purification (Akhter *et al.* 2022).

Modified TiO_2 photocatalysts have shown promising effects and mechanisms in degrading various types of dyes (Anucha *et al.* 2022). For instance, for azo dyes, modified TiO_2 photocatalysts can break the azo bonds and benzene ring structures of dye molecules by different pathways, such as direct adsorption, charge transfer, and free radical attack, resulting in the loss of color and toxicity of the dye molecules (Zhang *et al.* 2021a, 2021b, 2021c). For aromatic amine dyes, modified TiO_2 photocatalysts can cleave the aromatic amine structure by the free radical attack, hydroxyl substitution, etc., leading to the conversion of dye molecules into low-molecular-weight inorganic acids and water (Rauf *et al.* 2011). Different types of modified TiO_2 photocatalysts also exhibit different performances in degrading various types of dyes. For example, modified TiO_2 photocatalysts doped with metal or non-metal elements can enhance the light absorption ability and the separation efficiency of electron-hole pairs, thus improving the degradation efficiency (Basavarajappa *et al.* 2020). Modified TiO_2 photocatalysts that composite with other semiconductor materials can form heterojunction structures, which can extend the light response range and improve the charge transfer ability, thus improving the degradation efficiency (Wang *et al.* 2021).

One of the methods to modify TiO_2 for photocatalytic applications is to dope it with silver nanoparticles (Ag/TiO_2). Ag/TiO_2 can enhance the photocatalytic activity of TiO_2 by improving its light absorption, electron-hole separation, and

affinity toward organic pollutants. For example, Zhao *et al.* (2020) significantly improved the catalytic efficiency of TiO_2 under visible light by synergistically combining it with silver-covered carbon nanotubes (CA) to form a ternary structure called CNTs–Ag–TiO_2 (CAT). The composite underwent comprehensive characterization using various techniques, including XRD, SEM, X-ray photoelectron spectroscopy, diffuse reflectance spectra, and photoluminescence spectra. The researchers studied the photocatalytic activity of CAT using MB as a model pollutant to investigate the influence of CA content in the composite on photocatalysis. As depicted in Figure 3, the incorporation of CA into TiO_2 significantly enhanced its photocatalytic activity under both visible light and UV light. Notably, when the mass ratio of CA was 15%, the degradation rate of MB by CAT reached an impressive 80.8% under visible light within just 3 h, surpassing that of TiO_2 alone by a remarkable 16.5 times. Similarly, under UV light, the degradation rate reached 99.2% within a mere 40 min, which was almost twice as fast as that of TiO_2.

One type of modified TiO_2 photocatalyst that is widely used is CNT-doped TiO_2 (CNT/TiO_2). CNTs form a composite structure with TiO_2 that has close contact and provides a rapid electron transport channel. This reduces the recombination loss of electron-hole pairs and enhances the photocatalytic activity. Wang & Zhou (2011) conducted research to demonstrate the advantages of the composite photocatalyst CNTs/P-TiO_2, prepared through the hydrothermal method, over pure TiO_2. First, the CNTs/P-TiO_2 photocatalyst exhibits a smaller crystalline size, leading to enhanced photocatalytic activity. Second, it boasts a larger surface area, providing abundant active sites for the adsorption and degradation of pollutants. Third, it exhibits stronger absorption in the visible range, enabling the effective utilization of visible light for photocatalysis. As depicted in Figure 4, the CNTs/P-TiO_2 composite catalyst exhibits a synergistic effect in the photocatalytic degradation of methyl orange (MO) (a model organic pollutant). The combination of CNTs and phosphorus-doped TiO_2 results in significantly higher photocatalytic activity compared to pure TiO_2 and P25 (a commonly used commercial TiO_2 photocatalyst) under both UV and visible light irradiation.

The degradation of dye pollutants by modified TiO_2 photocatalysts depends on various factors. One of these factors is the pH value, which influences the ion balance and the surface charge state of water. These, in turn, affect the adsorption of dye molecules and modified TiO_2 photocatalysts (Rafiq *et al.* 2021). Another factor is the temperature, which influences the reaction rate and the equilibrium constant. These, in turn, affect the degradation kinetics and thermodynamics. A third factor is the additives, which influence the properties and the reaction mechanism of the reaction medium. These, in turn, affect the degradation effect. Therefore, it is necessary to select appropriate modified TiO_2 photocatalysts and optimize reaction parameters according to the specific water conditions and pollutant characteristics in practical applications, in order to achieve the optimal degradation effect (Han *et al.* 2009; Li *et al.* 2021a, 2021b).

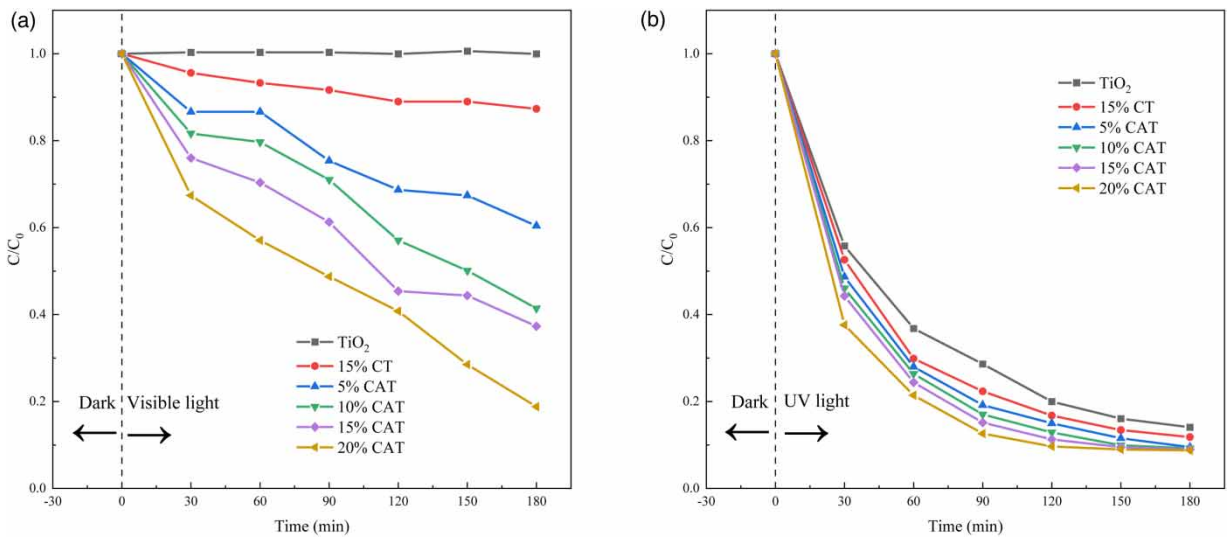


Figure 3 | Photocatalytic degradation of MB over the samples under (a) visible light irradiation and (b) UV light irradiation (Zhao *et al.* 2020).

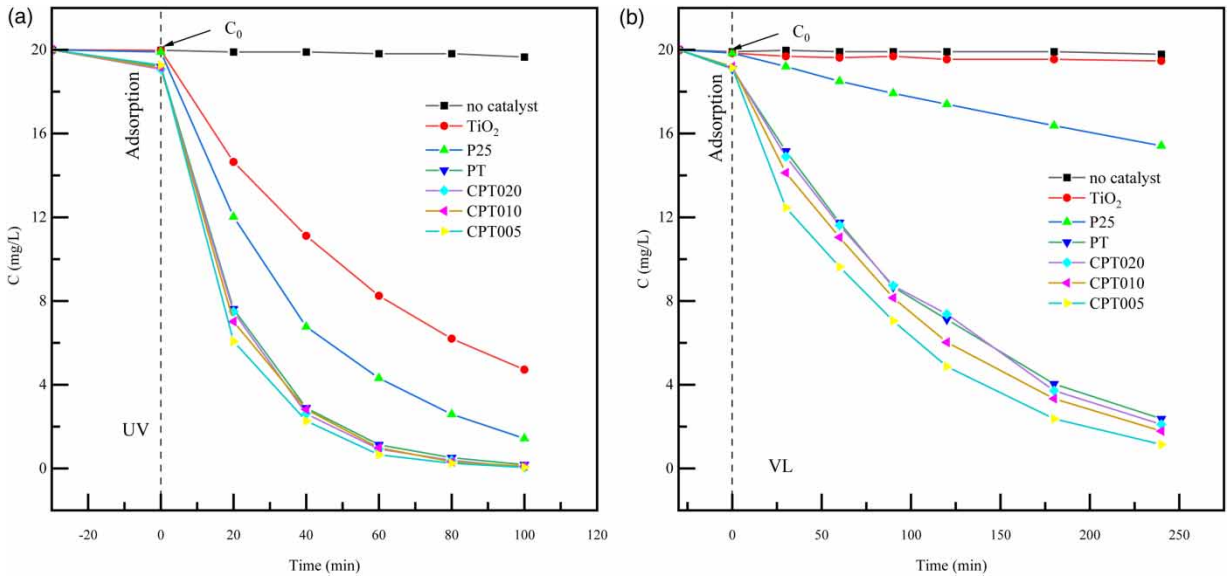


Figure 4 | Concentration variation of MO vs. irradiation time in the presence of various catalysts under (a) UV irradiation and (b) visible-light irradiation (Wang & Zhou 2011).

3.1.2. Pesticide pollutants

One of the major sources of organic pollutants in aquatic ecosystems is pesticides, which pose serious threats to both environmental and human health (Gwenzi & Chaukura 2018). A promising technique for degrading pesticide contaminants is the use of modified TiO_2 photocatalysts, which can harness solar or visible light to activate the modified TiO_2 surface and generate reactive free radicals. These radicals can oxidize and decompose pesticide molecules into harmless or low-toxic substances (Pelaez *et al.* 2012). Modified TiO_2 photocatalysts can be applied to various kinds of pesticides, such as herbicides and insecticides.

Song *et al.* (2021) focused on developing a highly efficient photoelectrocatalyst for the degradation of organic pollutants using a TiO_2 catalyst. Their research demonstrated the synthesis of TiO_2 nanocones, which exhibited superior performance and durability compared to other TiO_2 catalysts. As depicted in Figure 5, the nanocone catalyst showcased enhanced

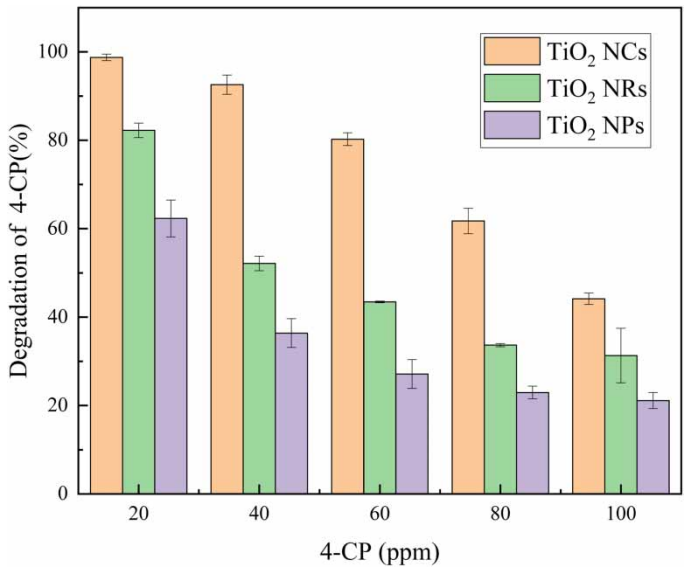


Figure 5 | Degradation of different concentrations of 4-CP on TiO_2 catalysts with different nanostructures (Song *et al.* 2021).

degradation performance for a specific organic pollutant, 4-chlorophenol (4-CP), achieving a degradation efficiency of 99% and a mineralization efficiency of over 55% at a concentration of 20 ppm. The apparent rate constant for the nanocone catalyst was found to be 5.05 h^{-1} g^{-1} m^2, which is significantly higher than that of nanorod and aggregated particle catalysts. The improved performance of the nanocone catalyst is attributed to its unique conical morphology, which enables the efficient separation and transfer of photo-generated charges, leading to enhanced photoelectrocatalytic (PEC) activity. Additionally, computational fluid dynamics simulations suggest that the three-dimensional conical structure facilitates mass transfer, further enhancing PEC performance. This research underscores the significance of nanometer-scale morphology tuning in photoelectrocatalysts for improved charge transfer and mass transportation, ultimately enhancing the PEC performance in the degradation of persistent pollutants. Anirudhan *et al.* (2020) developed a magnetic TiO_2 embedded molecularly imprinted polymer (mTiO_2-MIP) nanocomposite for the efficient degradation of diuron under visible light. Diuron, an environmental priority pollutant commonly found in water bodies due to pesticide overuse, served as the target compound for degradation. The primary objective of the study was to create a photocatalyst capable of effectively degrading diuron using visible light. The mTiO_2-MIP photocatalyst was synthesized by molecular imprinting on mTiO_2 using 3-thiophene acetic acid and 3-thiophene carboxaldehyde, forming a conducting layer of MIP. Various characterization techniques, including Fourier-transform infrared spectroscopy (FT-IR), XRD, SEM, TEM, vibrating sample magnetometer (VSM), UV–vis, diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry, and photoluminescence spectroscopy, were employed to analyze the nanocomposite. The MIP layer in the nanocomposite enhanced the catalyst's selectivity and acted as a photosensitizer. The study revealed that the mTiO_2-MIP photocatalyst exhibited superior photocatalytic degradation of diuron compared to mTiO_2 under visible light. The combination of magnetism and molecular imprinting technology with TiO_2 offered a novel and efficient approach for diuron degradation under visible light. In conclusion, the utilization of TiO_2, particularly in the form of the mTiO_2-MIP nanocomposite, proved to be effective in degrading pesticides like diuron under visible light conditions. The findings highlight the potential of this photocatalytic system for environmental remediation applications.

The degradation of pesticide pollutants by modified TiO_2 photocatalysts depends on various factors, such as pH, temperature, and additives. pH affects the surface charge of modified TiO_2 and the ionization degree of pesticide molecules, which influences their adsorption and reaction rate (Singh *et al.* 2023). Temperature determines the activity and stability of modified TiO_2 photocatalysts. The photocatalytic effect will decrease if the temperature is too high or too low. Additives can alter the structure, morphology, specific surface area, band structure, etc., of modified TiO_2 photocatalysts, which can enhance or reduce their photocatalytic activity. Therefore, it is necessary to choose appropriate modified TiO_2 photocatalysts and optimal reaction conditions according to the types of pesticide pollutants and water quality conditions to achieve the best degradation effect in practical applications.

3.1.3. Other organic pollutants

Modified TiO_2 is a photocatalyst that can degrade various organic pollutants in water, such as dyes, pesticides, phenols, benzenes, and surfactants. These pollutants are resistant to natural degradation and pose serious threats to water quality and ecology. Modified TiO_2 can utilize visible light or ultraviolet light to generate electron-hole pairs, which then produce reactive oxygen species (ROS), such as hydroxyl radicals ($^{\bullet}OH$) and superoxide radicals ($^{\bullet}O_2^-$). These ROS have high oxidative potential and can react with organic pollutants, transforming them into carbon dioxide and water and thus achieving water purification.

Eddy *et al.* (2021) conducted a study on the photocatalytic degradation of phenol using silica-modified TiO_2 as a composite photocatalyst. Phenol, a hazardous organic pollutant commonly found in industrial wastewater, poses significant risks to environmental and human health, making its removal crucial. In their research, they incorporated silica extracted from natural resources, such as beach sand, into the composite. The photocatalytic activity and characterization of the TiO_2/Si_2 composite were extensively investigated. Various techniques, including XRD, FT-IR, SEM, and particle size analysis, were employed to thoroughly characterize the composite. The study revealed that the composite exhibited high crystallinity and significantly improved photocatalytic activity compared to commercial TiO_2. Under UV irradiation, the optimized composite achieved a remarkable phenol degradation rate of 96.05% within 120 min, surpassing commercial TiO_2 by 3.5 times. The findings suggest that silica-modified TiO_2 holds great potential as an effective photocatalyst for phenol degradation in wastewater treatment applications.

In a study conducted by Murgolo *et al.*, SWCNTs-TiO_2 nanoparticles were utilized for the photodegradation of various organic pollutants, including pharmaceuticals such as warfarin, mefenamic acid, metoprolol, and carbamazepine. The

degradation rates of these pollutants were found to be comparable to those achieved with Degussa P25 TiO_2, a widely used photocatalyst. However, it was observed that the TiO_2 loading in the SWCNT–TiO_2 system was lower compared to Degussa P25 TiO_2. Moreover, when the photodegradation was performed in real wastewater samples, the efficiency of both catalysts decreased. In another study, multi-walled CNTs (MWCNTs) were combined with TiO_2 for the degradation of tetracycline antibiotic (TCL). The resulting MWCNT–TiO_2 nanocomposite exhibited the efficient degradation of TCL in both deionized water and real wastewater samples. The complete removal of TCL at concentrations up to 10 mg/dm^3 was achieved within 100 min of irradiation. While the efficiency decreased for higher TCL concentrations, low concentrations were still removed even after 10 min of irradiation. Additionally, the MWCNT–TiO_2 nanocomposite showed improved efficiency in reducing chemical oxygen demand (COD) and total organic carbon (TOC) in real wastewater samples compared to bare TiO_2. In summary, SWCNT–TiO_2 nanocomposites have demonstrated the effective degradation of organic pollutants, including pharmaceuticals. Their photocatalytic activity has been compared to traditional TiO_2 photocatalysts and has shown similar or improved efficiency in the removal of various organic pollutants, especially at lower concentrations (Krakowiak *et al.* 2021).

4. CONCLUSIONS

This paper systematically investigates the application of modified TiO_2 photocatalysts in the degradation of organic pollutants in water. Due to their environmentally friendly and high-efficiency characteristics, modified TiO_2 photocatalysts have gained significant attention as a promising water purification technology. By utilizing visible or ultraviolet light to generate active oxygen radicals, such as hydroxyl radicals and superoxide radicals, these catalysts can oxidize and degrade organic pollutants in water, effectively improving the water environment. The study first introduces different modification methods, including doping modification and semiconductor composite modification, and discusses their impacts on catalyst performance. The results demonstrate that modification is an effective approach to enhancing photocatalyst performance, increasing light absorption and electron-hole pair separation efficiency, and significantly improving the degradation efficiency of organic pollutants. Furthermore, this paper focuses on the application of modified TiO_2 photocatalysts in the degradation of dyes, pesticides, and other organic pollutants. The research results show that these catalysts exhibit excellent degradation efficiency for different types of organic pollutants. Concerning dye pollutants, modified TiO_2 catalysts can effectively break the chemical bonds of dye molecules, transforming them into harmless low-molecular-weight inorganic substances. For pesticide pollutants, modified TiO_2 catalysts can efficiently oxidize and degrade pesticide molecules, thereby effectively removing pollutants and purifying water environments. Lastly, this paper explores the factors affecting the degradation efficiency of modified TiO_2 photocatalysts. Factors such as pH, temperature, and additives significantly influence the surface charge of the catalyst and the adsorption and reaction rates of pollutants. Therefore, optimizing reaction parameters can further enhance the degradation efficiency in practical applications. Consequently, for specific water quality conditions and pollutant characteristics, selecting appropriate modified catalysts and optimal reaction conditions are essential to achieve the best degradation results. In conclusion, modified TiO_2 photocatalysts show tremendous potential and prospects in water treatment. This paper provides valuable references and guidance for in-depth research in this field, aiming to improve and optimize photocatalysis technology, enhance water purification efficiency, and promote environmentally friendly water treatment projects. Future research can further expand the application of modified TiO_2 photocatalysts in the treatment of different organic pollutants, advancing the practical implementation of this technology and making greater contributions to safeguarding water environments and maintaining ecological balance.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

Acharya, R. & Parida, K. 2020 A review on TiO_2/g-C_3N_4 visible-light-responsive photocatalysts for sustainable energy generation and environmental remediation. *Journal of Environmental Chemical Engineering* **8** (4), 103896.

Akhter, P., Arshad, A., Saleem, A. & Hussain, M. 2022 Recent development in non-metal-doped titanium dioxide photocatalysts for different dyes degradation and the study of their strategic factors: a review. *Catalysts* **12** (11), 1331.

Anirudhan, T., Christa, J. & Shainy, F. 2020 Magnetic titanium dioxide embedded molecularly imprinted polymer nanocomposite for the degradation of diuron under visible light. *Reactive and Functional Polymers* **152**, 104597.

Anitha, B. & Khadar, M. A. 2020 Anatase-rutile phase transformation and photocatalysis in peroxide gel route prepared TiO_2 nanocrystals: role of defect states. *Solid State Sciences* **108**, 106392.

Ansari, S. A., Khan, M. M., Ansari, M. O. & Cho, M. H. 2016 Nitrogen-doped titanium dioxide (N-doped TiO_2) for visible light photocatalysis. *New Journal of Chemistry* **40** (4), 3000–3009.

Anucha, C. B., Altin, I., Bacaksiz, E. & Stathopoulos, V. N. 2022 Titanium dioxide (TiO_2)-based photocatalyst materials activity enhancement for contaminants of emerging concern (CECs) degradation: in the light of modification strategies. *Chemical Engineering Journal Advances* **10**, 100262.

Arora, I., Chawla, H., Chandra, A., Sagadevan, S. & Garg, S. 2022 Advances in the strategies for enhancing the photocatalytic activity of TiO_2: conversion from UV-light active to visible-light active photocatalyst. *Inorganic Chemistry Communications* **143**, 109700.

Bagwasi, S., Niu, Y., Nasir, M., Tian, B. & Zhang, J. 2013 The study of visible light active bismuth modified nitrogen doped titanium dioxide photocatalysts: role of bismuth. *Applied Surface Science* **264**, 139–147.

Basavarajappa, P. S., Patil, S. B., Ganganagappa, N., Reddy, K. R., Raghu, A. V. & Reddy, C. V. 2020 Recent progress in metal-doped TiO_2, non-metal doped/codoped TiO_2 and TiO_2 nanostructured hybrids for enhanced photocatalysis. *International Journal of Hydrogen Energy* **45** (13), 7764–7778.

Bayan, E., Lupeiko, T., Pustovaya, L., Volkova, M., Butova, V. & Guda, A. 2020 Zn–F co-doped TiO_2 nanomaterials: synthesis, structure and photocatalytic activity. *Journal of Alloys and Compounds* **822**, 153662.

Cao, G., Deskins, N. A. & Yi, N. 2021 Carbon monoxide oxidation over copper and nitrogen modified titanium dioxide. *Applied Catalysis B: Environmental* **285**, 119748.

Chakraborty, I. & Pandey, A. 2023 A review article on application of ZnO-based nanocomposite materials in environmental remediation. *Materials Today: Proceedings*. https://doi.org/10.1016/j.matpr.2023.02.041 (accessed 7 September 2023).

Chen, X., Peng, X., Jiang, L., Yuan, X., Zhang, J. & Yu, H. 2020 Terephthalate acid decorated TiO_2 for visible light driven photocatalysis mediated via ligand-to-metal charge transfer (LMCT). *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **603**, 125188.

Cheng, X., Yu, X., Xing, Z. & Yang, L. 2016 Synthesis and characterization of N-doped TiO_2 and its enhanced visible-light photocatalytic activity. *Arabian Journal of Chemistry* **9**, S1706–S1711.

Dong, B., Liu, T., Li, C. & Zhang, F. 2018 Species, engineering and characterizations of defects in TiO_2-based photocatalyst. *Chinese Chemical Letters* **29** (5), 671–680.

Eddy, D. R., Ishmah, S. N., Permana, M. D., Firdaus, M. L., Rahayu, I., El-Badry, Y. A., Hussein, E. E. & El-Bahy, Z. M. 2021 Photocatalytic phenol degradation by silica-modified titanium dioxide. *Applied Sciences* **11** (19), 9033.

Fadillah, G., Hidayat, R. & Saleh, T. A. 2022 Hydrothermal assisted synthesis of titanium dioxide nanoparticles modified graphene with enhanced photocatalytic performance. *Journal of Industrial and Engineering Chemistry* **113**, 411–418.

Fawzi, T., Rani, S., Roy, S. C. & Lee, H. 2022 Photocatalytic carbon dioxide conversion by structurally and materially modified titanium dioxide nanostructures. *International Journal of Molecular Sciences* **23** (15), 8143.

Gao, Y., Liu, F., Chi, X., Tian, Y., Zhu, Z., Guan, R. & Song, J. 2022 A mesoporous nanofibrous $BiVO_4$-Ni/$AgVO_3$ Z-scheme heterojunction photocatalyst with enhanced photocatalytic reduction of Cr^{6+} and degradation of RhB under visible light. *Applied Surface Science* **603**, 154416.

Gavrilescu, M. 2021 Water, soil, and plants interactions in a threatened environment. *Water* **13** (19), 2746.

Gwenzi, W. & Chaukura, N. 2018 Organic contaminants in African aquatic systems: current knowledge, health risks, and future research directions. *Science of the Total Environment* **619**, 1493–1514.

Han, F., Kambala, V. S. R., Srinivasan, M., Rajarathnam, D. & Naidu, R. 2009 Tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater treatment: a review. *Applied Catalysis A: General* **359** (1–2), 25–40.

Ismail, M., Akhtar, K., Khan, M., Kamal, T., Khan, M. A., Asiri A, M., Seo, J. & Khan, S. B. 2019 Pollution, toxicity and carcinogenicity of organic dyes and their catalytic bio-remediation. *Current Pharmaceutical Design* **25** (34), 3645–3663.

Jeon, J. P., Kweon, D. H., Jang, B. J., Ju, M. J. & Baek, J. B. 2020 Enhancing the photocatalytic activity of TiO_2 catalysts. *Advanced Sustainable Systems* **4** (12), 2000197.

Jiang, D., Otitoju, T. A., Ouyang, Y., Shoparwe, N. F., Wang, S., Zhang, A. & Li, S. 2021 A review on metal ions modified TiO_2 for photocatalytic degradation of organic pollutants. *Catalysts* **11** (9), 1039.

Krakowiak, R., Musial, J., Bakun, P., Spychała, M., Czarczynska-Goslinska, B., Mlynarczyk, D. T., Koczorowski, T., Sobotta, L., Stanisz, B. & Goslinski, T. 2021 Titanium dioxide-based photocatalysts for degradation of emerging contaminants including pharmaceutical pollutants. *Applied Sciences* **11** (18), 8674.

Li, X., Raza, S. & Liu, C. 2021a Preparation of titanium dioxide modified biomass polymer microspheres for photocatalytic degradation of rhodamine-B dye and tetracycline. *Journal of the Taiwan Institute of Chemical Engineers* **122**, 157–167.

Li, Z., Luo, L., Li, M., Chen, W., Liu, Y., Yang, J., Xu, S.-M., Zhou, H., Ma, L. & Xu, M. 2021b Photoelectrocatalytic C–H halogenation over an oxygen vacancy-rich TiO_2 photoanode. *Nature Communications* **12** (1), 6698.

Li, Z., Wang, S., Wu, J. & Zhou, W. 2022 Recent progress in defective TiO_2 photocatalysts for energy and environmental applications. *Renewable and Sustainable Energy Reviews* **156**, 111980.

Liu, G., Yang, H. G., Pan, J., Yang, Y. Q., Lu, G. Q. & Cheng, H.-M. 2014 Titanium dioxide crystals with tailored facets. *Chemical Reviews* **114** (19), 9559–9612.

Liu, T., Chen, W., Liu, X., Zhu, J. & Lu, L. 2016 Well-dispersed ultrafine nitrogen-doped TiO_2 with polyvinylpyrrolidone (PVP) acted as N-source and stabilizer for water splitting. *Journal of Energy Chemistry* **25** (1), 1–9.

Liu, G., Wang, G., Hu, Z., Su, Y. & Zhao, L. 2019 Ag_2O nanoparticles decorated TiO_2 nanofibers as a pn heterojunction for enhanced photocatalytic decomposition of RhB under visible light irradiation. *Applied Surface Science* **465**, 902–910.

Liu, H., Wang, C. & Wang, G. 2020 Photocatalytic advanced oxidation processes for water treatment: recent advances and perspective. *Chemistry – An Asian Journal* **15** (20), 3239–3253.

Ma, S., Lee, S., Kim, K., Im, J. & Jeon, H. 2021 Purification of organic pollutants in cationic thiazine and azo dye solutions using plasma-based advanced oxidation process via submerged multi-hole dielectric barrier discharge. *Separation and Purification Technology* **255**, 117715.

Muangmora, R., Kemacheevakul, P. & Chuangchote, S. 2021 Titanium dioxide and its modified forms as photocatalysts for air treatment. *Current Analytical Chemistry* **17** (2), 185–201.

Mushtaq, N., Singh, D. V., Bhat, R. A., Dervash, M. A. & Hameed, O. B. 2020 Freshwater contamination: Sources and hazards to aquatic biota. In: Qadri, H., Bhat, R., Mehmood, M., Dar, G. (eds) *Fresh Water Pollution Dynamics and Remediation*. Springer, Singapore, pp. 27–50.

Niu, B., Wang, X., Wu, K., He, X. & Zhang, R. 2018 Mesoporous titanium dioxide: synthesis and applications in photocatalysis, energy and biology. *Materials* **11** (10), 1910.

Pelaez, M., Nolan, N. T., Pillai, S. C., Seery, M. K., Falaras, P., Kontos, A. G., Dunlop, P. S., Hamilton, J. W., Byrne, J. A. & O'shea, K. 2012 A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Applied Catalysis B: Environmental* **125**, 331–349.

Qahtan, T. F., Owolabi, T. O. & Saleh, T. A. 2023 2000-eV argon ion beam induced formation of multiple chemical states in titanium dioxide mesoporous film. *Ceramics International* **49** (18), 30273–30279.

Rafiq, A., Ikram, M., Ali, S., Niaz, F., Khan, M., Khan, Q. & Maqbool, M. 2021 Photocatalytic degradation of dyes using semiconductor photocatalysts to clean industrial water pollution. *Journal of Industrial and Engineering Chemistry* **97**, 111–128.

Rauf, M., Meetani, M. & Hisaindee, S. 2011 An overview on the photocatalytic degradation of azo dyes in the presence of TiO_2 doped with selective transition metals. *Desalination* **276** (1–3), 13–27.

Sedrati, H., Bensaha, R., Bensouyad, H., Miska, P. & Robert, S. 2014 Structural, optical and waveguiding properties improvement of SiO_2/TiO_2 Bragg reflectors processed by the sol–gel method under the effect of Ni-doped TiO_2 and annealing duration. *Materials Research Bulletin* **57**, 287–292.

Singh, J., Yadav, P., Pal, A. K. & Mishra, V. 2020 Water pollutants: Origin and status. In: Pooja, D., Kumar, P., Singh, P., Patil, S. (eds) *Sensors in Water Pollutants Monitoring: Role of Material. Advanced Functional Materials and Sensors*. Springer, Singapore, pp. 5–20.

Singh, S. K., Mishra, P. K. & Upadhyay, S. N. 2023 Recent developments in photocatalytic degradation of insecticides and pesticides. *Reviews in Chemical Engineering* **39** (2), 225–270.

Song, R., Chi, H., Ma, Q., Li, D., Wang, X., Gao, W., Wang, H., Wang, X., Li, Z. & Li, C. 2021 Highly efficient degradation of persistent pollutants with 3D nanocone TiO_2-based photoelectrocatalysis. *Journal of the American Chemical Society* **143** (34), 13664–13674.

Stojadinović, S., Radić, N., Tadić, N., Vasilić, R. & Tsanev, A. 2022 TiO_2/Bi_2O_3 coatings formed by plasma electrolytic oxidation of titanium for photocatalytic applications. *Journal of Materials Science: Materials in Electronics* **33** (7), 4467–4481.

Subhiksha, V., Kokilavani, S. & Khan, S. S. 2022 Recent advances in degradation of organic pollutant in aqueous solutions using bismuth based photocatalysts: a review. *Chemosphere* **290**, 133228.

Turkten, N. & Bekbolet, M. 2020 Doped TiO_2 photocatalysts for the photocatalytic degradation efficiency of methylene blue and humic acid under solar light. *Hittite Journal of Science and Engineering* **7** (2), 109–114.

Wang, S. & Zhou, S. 2011 Photodegradation of methyl orange by photocatalyst of CNTs/P-TiO_2 under UV and visible-light irradiation. *Journal of Hazardous Materials* **185** (1), 77–85.

Wang, W., Zhang, D., Ji, Z., Shao, D., Sun, P. & Duan, J. 2021 High efficiency photocatalytic degradation of indoor formaldehyde with silver-doped ZnO/g-C_3N_4 composite catalyst under the synergistic effect of silver plasma effect and heterojunction. *Optical Materials* **111**, 110721.

Wang, G., Lv, S., Shen, Y., Li, W., Lin, L. & Li, Z. 2023 Advancements in heterojunction, cocatalyst, defect and morphology engineering of semiconductor oxide photocatalysts. *Journal of Materiomics*. https://doi.org/10.1016/j.jmat.2023.05.014 (accessed 7 September 2023).

Yao, H., Zhang, Y., He, S., Zuo, H. & Feng, G. 2023 New insight into the enhanced photocatalytic activity of Al-, C-and Al-C co-doped rutile TiO_2 photocatalysts. *Materials Today Communications* **36**, 106763.

Zhang, W., He, H., Tian, Y., Lan, K., Liu, Q., Wang, C., Liu, Y., Elzatahry, A., Che, R. & Li, W. 2019 Synthesis of uniform ordered mesoporous TiO_2 microspheres with controllable phase junctions for efficient solar water splitting. *Chemical Science* **10** (6), 1664–1670.

Zhang, G., Liu, Y., Hashisho, Z., Sun, Z., Zheng, S. & Zhong, L. 2020 Adsorption and photocatalytic degradation performances of TiO_2/diatomite composite for volatile organic compounds: effects of key parameters. *Applied Surface Science* **525**, 146633.

Zhang, C., Chen, H., Xue, G., Liu, Y., Chen, S. & Jia, C. 2021a A critical review of the aniline transformation fate in azo dye wastewater treatment. *Journal of Cleaner Production* **321**, 128971.

Zhang, L.-Y., Han, Y.-L., Yang, J.-J., Deng, S.-L. & Wang, B.-Y. 2021b Construction and photocatalysis of carbon quantum dots/layered mesoporous titanium dioxide (CQDs/LM-TiO_2) composites. *Applied Surface Science* **546**, 149089.

Zhang, Y., Zhang, Y., Huang, Y., Jia, Y., Chen, L., Pan, Y. & Wang, M. 2021c Adsorptive-photocatalytic performance and mechanism of Me (Mn, Fe)-N co-doped TiO_2/SiO_2 in cyanide waste. *Journal of Alloys and Compounds* **867**, 159020.

Zhao, C., Guo, J., Yu, C., Zhang, Z., Sun, Z. & Piao, X. 2020 Fabrication of CNTs-Ag-TiO_2 ternary structure for enhancing visible light photocatalytic degradation of organic dye pollutant. *Materials Chemistry and Physics* **248**, 122873.

First received 30 April 2023; accepted in revised form 25 August 2023. Available online 6 September 2023