

Black titanium dioxide toward sustainable water purification: Fundamentals, structure engineering, and future perspectives

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Abstract: Black titanium dioxide (TiO₂) has emerged as a promising visible-light-responsive photocatalyst for water purification owing to its defect-rich structure, which enhances light harvesting and charge separation. This review summarized recent advances in the structural characteristics, preparation strategies, photocatalytic mechanisms, and structure engineering of black TiO₂. Its applications in degrading conventional organic pollutants and emerging contaminants were highlighted, together with challenges associated with real wastewater treatment. Current limitations regarding defect stability, mechanistic understanding, catalyst recovery, and performance evaluation were critically discussed. Finally, future perspectives, including precise defect engineering, operando characterization, data-driven catalyst design, and continuous-flow photocatalytic systems, were proposed to facilitate the practical application of black TiO₂ in sustainable water purification.

1. Introduction

The continuous discharge of refractory organic pollutants, including dyes, antibiotics, phenolic compounds, pesticides, endocrine-disrupting chemicals (EDCs), and pharmaceuticals and personal care products (PPCPs), has become a major threat to aquatic ecosystems and human health because of their high stability, poor biodegradability, and potential toxicity [1-3]. In response, increasingly stringent environmental regulations, such as the United Nations Sustainable Development Goal 6 [4] and the European Union Water Framework Directive [5], have emphasized the development of efficient and sustainable water treatment technologies.

Among various remediation strategies, semiconductor photocatalysis has attracted considerable attention because it directly utilizes solar energy to generate photogenerated electrons, holes, and reactive oxygen species (ROS, including hydroxyl radicals ($\cdot\text{OH}$), superoxide radicals ($\cdot\text{O}_2^-$), and singlet oxygen ($^1\text{O}_2$)), enabling the degradation and even complete mineralization of organic pollutants under mild conditions [6]. Compared with conventional treatment technologies, photocatalysis offers advantages such as low energy consumption, minimal secondary pollution, and broad applicability, making it one of the most promising advanced oxidation technologies for water purification [7].

TiO₂ is one of the most extensively studied photocatalysts owing to its low cost, excellent chemical stability, non-toxicity, and strong resistance to photocorrosion [8]. However, its practical application is hindered by the wide band gaps of anatase (3.2 eV) and rutile (3.0 eV), which limit light absorption mainly to the ultraviolet region, together with the rapid recombination of photogenerated electron–hole pairs [9]. Therefore, extending visible-light utilization and improving charge separation have become key objectives in TiO₂ photocatalysis.

A breakthrough was reported by Chen et al. in 2011 with the development of hydrogenated black TiO₂ [10], significantly enhancing solar absorption by introducing disorder in surface layers of nanophase TiO₂ through hydrogenation. The relevant photos and high-resolution transmission electron microscopy of samples are depicted in Figure 1. Unlike pristine TiO₂, black TiO₂ is a defect-engineered material containing abundant Ti³⁺ species, oxygen vacancies (OVs), hydrogen-related defects, and surface-disordered layers. These defect structures effectively regulate the electronic structure, broaden light absorption from the ultraviolet to the visible region, and facilitate charge transfer, resulting in significantly enhanced photocatalytic activity [11]. Nevertheless, photocatalytic performance is determined not simply by the presence of defects but by their type, concentration, spatial distribution, and interaction with the crystal framework.

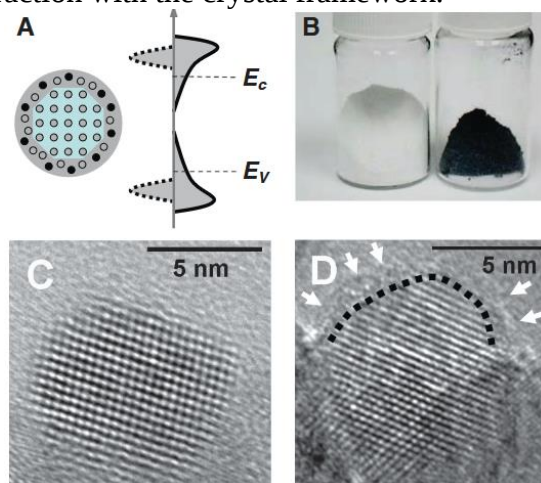


Figure 1: (A) Schematic illustration of the structure and electronic DOS of a semiconductor in the form of a disorder-engineered nanocrystal with dopant incorporation, (B) A photo comparing unmodified white and disorder-engineered black TiO₂ nanocrystals, (C and D) HRTEM images of TiO₂ nanocrystals before and after hydrogenation, respectively [10].

This review summarized recent advances in black TiO₂ for photocatalytic degradation of organic pollutants in water. Emphasis was placed on its structural characteristics, preparation strategies, charge-transfer mechanisms, structure engineering, and applications in water purification. Current challenges and future perspectives were also discussed to provide guidance for the rational design of efficient and sustainable black TiO₂ photocatalysts.

2. Structural features and preparation of black TiO₂

2.1 Structural characteristics

Black TiO₂ is generally regarded as a defect-engineered form of conventional TiO₂ rather than a new crystalline phase. It can be derived from anatase, rutile, brookite, or mixed-phase TiO₂ while largely preserving the original crystal framework after reduction [12]. Its enhanced photocatalytic performance mainly originates from Ti³⁺ species, OVs, and surface-disordered structures. During reduction, electrons released by lattice oxygen removal are trapped by neighboring Ti⁴⁺ ions,

producing Ti^{3+} centers (Equation 1), while the loss of lattice oxygen simultaneously generates OVs according to the Kröger–Vink notation (Equation 2). These coupled defects introduce localized electronic states, improve electrical conductivity, promote charge transfer, and provide abundant active sites for the adsorption and activation of O_2 , H_2O , and organic pollutants. However, excessive Ti^{3+} or OVs may create deep trap states that accelerate electron-hole recombination, indicating that photocatalytic activity depends on optimized defect concentration and spatial distribution rather than defect density alone.



Many black TiO_2 materials also exhibit a crystalline core-disordered shell structure. The defect-rich surface layer, containing distorted TiO_6 bonds, undercoordinated Ti atoms, hydroxyl groups, Ti^{3+} species, and OVs, broadens visible-light absorption, enhances surface adsorption, and facilitates interfacial charge transfer and ROS generation [13]. Nevertheless, these beneficial effects arise from the synergistic interaction between defect chemistry and the crystalline framework. Although the improved visible-light response is often attributed to band-gap narrowing, increasing evidence suggests that it primarily originates from defect-induced electronic states rather than an intrinsic reduction of the TiO_2 band gap.

2.2 Preparation strategies

Various strategies have been developed to prepare black TiO_2 , which can be broadly classified into hydrogen reduction, chemical reduction, electrochemical reduction, and emerging preparation methods, as seen in Table 1.

2.2.1 Hydrogen reduction

Hydrogen reduction is the most representative approach for producing black TiO_2 and includes both high-pressure and atmospheric-pressure treatments [14]. During hydrogenation, partial removal of lattice oxygen and hydrogen incorporation generate Ti^{3+} species, OVs, and a surface-disordered layer, thereby extending light absorption into the visible region [15]. Compared with high-pressure hydrogenation, atmospheric reduction using H_2/Ar , H_2/N_2 , NH_3 , CO , or forming gas is easier to implement and offers greater flexibility in defect regulation. However, excessive reduction temperatures or prolonged treatment may induce grain growth and defect diffusion, highlighting the need to optimize crystallinity and defect concentration.

2.2.2 Chemical reduction

Chemical reduction is widely used because of its simplicity, mild conditions, and low cost. Common reductants include NaBH_4 , CaH_2 , MgH_2 , TiH_2 , metallic Al and Zn, as well as organic reductants such as glucose and polyols. These reagents generate Ti^{3+} species and OVs by removing lattice oxygen without requiring hydrogen gas [16]. Among them, NaBH_4 is the most frequently employed due to its strong reducing capability and broad applicability to powders, nanotubes, and thin films [17]. Nevertheless, excessive reduction may produce lower titanium oxides or residual impurities, requiring careful control of reaction conditions and post-treatment.

2.2.3 Electrochemical reduction

Electrochemical reduction is particularly suitable for TiO_2 nanotube arrays and thin-film electrodes. Cathodic polarization converts Ti^{4+} into Ti^{3+} while simultaneously generating OVs near the electrode

surface. This method enables precise control of defect concentration through the applied potential and reduction time, without the need for external reducing agents [18]. However, it is mainly applicable to conductive substrates rather than free-standing powder photocatalysts.

2.2.4 Emerging preparation methods

Emerging approaches, including plasma treatment, laser irradiation, ion-beam bombardment, and hydrothermal/solvothermal self-reduction, provide alternative routes for defect engineering. Physical methods rapidly generate surface defects with minimal damage to the crystal lattice, whereas self-reduction introduces Ti^{3+} species and OV_s during crystal growth under relatively mild conditions. Although these techniques offer improved flexibility and controllability, their practical applications are still limited by equipment cost, scalability, or complex defect chemistry [19]. Overall, future efforts should focus on developing scalable, energy-efficient synthesis strategies capable of precisely regulating defect structures while maintaining high structural stability.

Table 1: Comparison of representative preparation methods for black TiO_2

Method	Typical Conditions	Main Defects	Advantages	Limitations	Representative Applications
High-pressure hydrogenation	High temperature, high-pressure H_2	Ti^{3+} , OV _s , disordered shell	Strong visible-light absorption; stable defect structure	High cost; safety concerns; difficult scale-up	Powder photocatalysts, H_2 evolution
Atmospheric hydrogenation/reductive annealing	H_2/Ar , H_2/N_2 , CO , NH_3	Ti^{3+} , OV _s	Simple operation; tunable reduction conditions	Grain growth; defect diffusion at high temperature	Organic pollutant degradation
Chemical reduction	NaBH_4 , CaH_2 , MgH_2 , glucose, glycerol	Ti^{3+} , OV _s	Mild conditions; low cost; suitable for various morphologies	Residual impurities; possible over-reduction	Powders, nanotubes, thin films
Electrochemical reduction	Cathodic polarization	Surface Ti^{3+} , OV _s	Precise defect control; suitable for immobilized electrodes	Mainly applicable to films and nanotubes	Photoelectrocatalysis
Plasma/laser/ion irradiation	H_2 plasma, Ar plasma, laser, ion beam	Surface defects	Localized modification; minimal bulk damage	High equipment cost; limited scalability	Fundamental defect engineering
Hydrothermal/solvothermal self-reduction	Organic solvents or reductants	Ti^{3+} , OV _s	Mild synthesis; simultaneous morphology control	Complex defect chemistry; possible carbon doping	Nanostructured photocatalysts

3. Structure engineering and photocatalytic mechanism

3.1 Charge transfer mechanism

The superior photocatalytic performance of black TiO_2 arises from the synergistic effects of enhanced visible-light absorption, efficient charge separation, and accelerated surface redox reactions

[20]. Under light irradiation, electrons are excited from the valence band (VB) or defect-induced states to the conduction band (CB), leaving holes in the VB (Equation 3):



Compared with pristine TiO_2 , black TiO_2 contains abundant Ti^{3+} species, OV, and surface-disordered structures, which introduce localized defect states, broaden visible-light absorption, and facilitate charge migration. However, defect engineering requires a delicate balance, as excessive defects may become recombination centers and reduce carrier lifetime.

Photogenerated electrons and holes subsequently participate in surface redox reactions to generate ROS. Electrons reduce dissolved oxygen to produce $\cdot\text{O}_2^-$ radicals (Equation 4), which can be further converted into hydroperoxyl radicals ($\text{HO}_2\cdot$, Equation 5), H_2O_2 (Equation 6), and $\cdot\text{OH}$ (Equation 7), while holes directly oxidize pollutants or react with $\text{H}_2\text{O}/\text{OH}^-$ to generate $\cdot\text{OH}$ (Equation 8). Depending on the catalyst structure and reaction conditions, singlet oxygen ($^1\text{O}_2$) may also contribute to pollutant oxidation. The dominant ROS depend on multiple factors, including band-edge positions, defect distribution, catalyst composition, dissolved oxygen, solution pH, irradiation wavelength, and the presence of cocatalysts or heterojunctions.



Photocatalytic degradation generally involves pollutant adsorption, charge separation, ROS generation, and sequential oxidation, ultimately converting organic pollutants into CO_2 , H_2O , and inorganic ions, as shown in Figure 2. Since pollutant removal does not necessarily indicate complete mineralization or detoxification, photocatalytic performance should be comprehensively evaluated using total organic carbon (TOC) removal, intermediate identification by liquid chromatography–mass spectrometry (LC–MS), and toxicity assessment, rather than relying solely on decolorization or UV–Vis analysis.

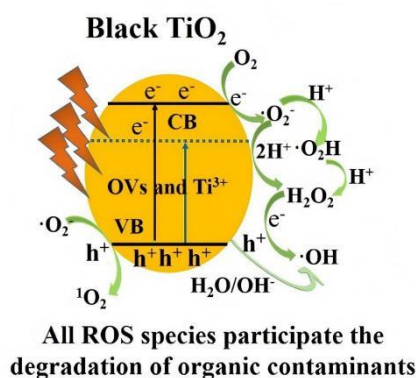


Figure 2: The generation of charge carriers and further ROS species in black TiO_2

3.2 Structure engineering strategies

Although defect engineering effectively enhances the visible-light response of black TiO_2 , additional structure engineering is often required to further improve charge separation, interfacial reactions, and catalyst stability.

Various modification strategies have been developed, including noble-metal deposition, elemental doping, heterojunction construction, and catalyst immobilization [21]. Noble metals (e.g., Ag, Au, Pt, and Pd) act as electron sinks through Schottky junctions, while plasmonic metals additionally enhance visible-light absorption via localized surface plasmon resonance. Transition- and nonmetal dopants regulate the electronic structure, optimize defect chemistry, and improve charge transport. Heterojunctions constructed with semiconductors, carbon materials, or MOF-derived materials generate built-in electric fields that facilitate charge separation, whereas immobilization on substrates such as glass, titanium, ceramics, or membranes improves catalyst recovery and enables continuous-flow operation.

Despite their different architectures, these strategies share the common objective of maximizing charge utilization and accelerating interfacial redox reactions. Recently, advanced interface engineering, including heterojunctions with different types in Figure 3 [22], defect–interface coupling, and single-atom cocatalysts, has attracted considerable attention because of their ability to simultaneously enhance light harvesting, charge separation, and photocatalytic activity.

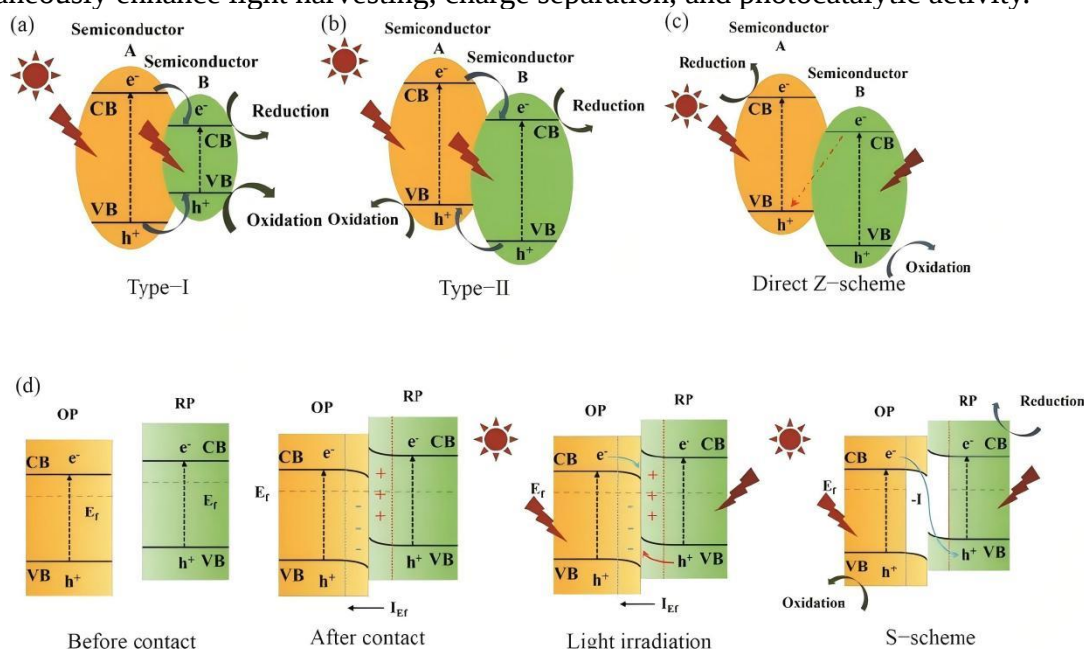


Figure 3: Traditional generation and transfer of charge carriers in heterojunctions: (a) Type-I, (b) Type-II, (c) direct Z-scheme, (d) S-scheme [22]

Nevertheless, each modification strategy also presents limitations. Excessive noble-metal loading increases cost and may shield active sites, inappropriate dopant concentrations can introduce recombination centers, and heterojunction mechanisms often require comprehensive characterization beyond band alignment. Although immobilized photocatalysts facilitate catalyst recovery, they generally suffer from reduced surface area and mass-transfer limitations. Therefore, future structure engineering should emphasize the synergistic optimization of defect structures, interface quality, and catalyst stability to maximize photocatalytic performance.

4. Applications in water purification

4.1 Conventional organic pollutants

Conventional organic pollutants have long served as model compounds for evaluating photocatalytic activity because of their well-defined structures and readily measurable degradation

behavior. Among them, dyes and phenolic compounds are the most extensively investigated and provide valuable insights into the intrinsic photocatalytic performance of black TiO₂.

4.1.1 Dyes

Organic dyes, such as methylene blue (MB), rhodamine B (RhB), methyl orange (MO), Congo red (CR), and crystal violet (CV), are widely used because their degradation can be conveniently monitored by UV–Vis spectroscopy [23]. Benefiting from enhanced visible-light absorption and improved charge separation, black TiO₂ generally exhibits superior dye degradation compared with pristine TiO₂. However, photosensitive dyes, particularly RhB and MB, may undergo dye-sensitized degradation by injecting excited electrons into TiO₂, resulting in an overestimation of photocatalytic activity. Therefore, dye degradation should be regarded as a preliminary evaluation and complemented by colorless pollutants to assess the intrinsic visible-light activity of black TiO₂.

4.1.2 Phenolic compounds

Phenolic compounds, including phenol and p-nitrophenol, are widely accepted as representative colorless pollutants because they exhibit negligible photosensitization and relatively stable aromatic structures. Their degradation typically proceeds through hydroxylation, aromatic ring opening, and mineralization. Compared with dyes, phenolic compounds provide a more reliable platform for investigating photocatalytic mechanisms, ROS generation, and structure–activity relationships.

4.2 Emerging contaminants

4.2.1 Antibiotics

Antibiotics, such as tetracycline (TC), ciprofloxacin (CIP), sulfamethoxazole (SMX), norfloxacin (NOR), and amoxicillin (AMX), are representative emerging contaminants because of their persistence and potential contribution to antimicrobial resistance. Owing to their complex molecular structures, degradation often produces multiple intermediates [24]. Consequently, catalyst performance should be evaluated using not only pollutant removal but also TOC mineralization, LC–MS analysis, residual antibacterial activity, ecotoxicity, and the potential formation of antibiotic resistance genes.

4.2.2 Pharmaceuticals and personal care products

PPCPs compounds, including ibuprofen, diclofenac, carbamazepine, and acetaminophen, are continuously released into aquatic environments and are poorly removed by conventional treatment processes. Black TiO₂ has shown promising visible-light activity toward these pollutants; however, most studies are still conducted at concentrations much higher than those found in natural waters. Future research should therefore focus on environmentally relevant concentrations and realistic treatment conditions.

4.2.3 Endocrine-disrupting chemicals

Representative EDCs, such as bisphenol A (BPA), phthalate esters, and alkylphenols, possess high chemical stability and weak photosensitization, making them suitable model contaminants for evaluating intrinsic photocatalytic activity. Since degradation may generate toxic intermediates, comprehensive product identification and toxicity assessment are essential. Black TiO₂ has also been explored for microplastic degradation, although practical applications remain limited.

4.3 Practical challenges

Despite encouraging laboratory results, practical water treatment remains challenging. Most studies are performed in simulated solutions rather than real wastewater, where coexisting inorganic ions and natural organic matter (NOM) may compete for active sites, consume ROS, and reduce photocatalytic efficiency. In addition, high pollutant removal does not necessarily indicate complete detoxification, as toxic intermediates may still be generated. Therefore, catalyst performance should be comprehensively evaluated using TOC mineralization, LC–MS, and ecotoxicity analyses instead of removal efficiency alone. Future studies should further emphasize continuous-flow reactors, real wastewater, environmentally relevant pollutant concentrations, and long-term catalyst stability to facilitate the practical application of black TiO₂.

5. Challenges and future perspectives

5.1 Remaining challenges

Despite the rapid development of black TiO₂, several challenges still hinder its practical application in water purification. The first concerns the stability of defect structures. Ti³⁺ species and OV_s, which are responsible for enhanced visible-light activity, are thermodynamically unstable and can be gradually oxidized during long-term exposure to air, water, or illumination, leading to deteriorated photocatalytic performance. Therefore, long-term durability should be evaluated beyond a few recycling tests.

Another challenge is the uncertain role of defects. Although Ti³⁺ species and OV_s generally promote visible-light absorption, charge separation, and ROS generation, excessive defects may also act as recombination centers. Moreover, the origin of the enhanced visible-light response remains controversial, with mechanisms including defect-state excitation, surface disorder, free-carrier absorption, and band-gap narrowing still under debate.

The lack of standardized evaluation protocols also limits meaningful comparison among different studies. Photocatalytic performance is commonly assessed only by pollutant removal using high-concentration dye solutions, whereas mineralization efficiency, intermediate toxicity, catalyst stability, and realistic irradiation conditions are often overlooked.

Finally, catalyst recovery and engineering implementation remain major obstacles. Powder photocatalysts are difficult to separate and reuse, while immobilized catalysts often suffer from reduced surface area and mass-transfer limitations. Developing efficient, reusable, and scalable photocatalytic systems is therefore essential for practical applications.

5.2 Future perspectives

Future research should focus on improving both the fundamental understanding and practical applicability of black TiO₂. Defect engineering should evolve from increasing defect concentration to precise regulation of defect type, concentration, energy level, and spatial distribution to maximize charge separation while minimizing carrier recombination.

Advanced operando characterization techniques, including In-situ EPR, XPS, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), transient spectroscopy, and isotope-labeling experiments, combined with DFT results, are expected to provide deeper insights into defect evolution, charge transfer, and photocatalytic mechanisms. In addition, machine learning and data-driven materials design offer new opportunities to correlate synthesis conditions with defect characteristics and catalytic performance, accelerating the rational design of high-performance photocatalysts.

From an engineering perspective, greater attention should be devoted to immobilized photocatalysts and continuous-flow reactors, such as nanotube arrays, photocatalytic membranes, and porous monolithic supports, to improve catalyst recovery and facilitate large-scale water treatment. Meanwhile, standardized evaluation protocols should be established by incorporating photon flux, TOC mineralization, intermediate identification, catalyst stability, and toxicity assessment. More importantly, future studies should validate catalyst performance in real wastewater containing natural organic matter and coexisting inorganic ions, thereby bridging the gap between laboratory research and practical environmental applications.

6. Conclusions

Black TiO₂ has emerged as a promising visible-light-responsive photocatalyst owing to its defect-rich structure, which enhances light harvesting and charge separation. Recent advances demonstrate that defect engineering combined with elemental doping, heterojunction construction, and catalyst immobilization can significantly improve the degradation of organic pollutants. Nevertheless, practical applications remain limited by defect instability, unclear photocatalytic mechanisms, insufficient evaluation standards, and engineering challenges. Future efforts should focus on precise defect regulation, operando characterization, AI-assisted catalyst design, and continuous-flow systems, together with validation under realistic wastewater conditions, to facilitate the practical implementation of black TiO₂ for sustainable water purification.

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