

Research Progress of TiO₂ Modification and Photodegradation of Organic Pollutants

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Abstract: Titanium dioxide (TiO₂) photocatalysts, characterized by exceptional photocatalytic activity, high photoelectric conversion efficiency, and economic viability, have found widespread application in recent years for azo dye degradation. However, inherent constraints, such as the material's limited visible light absorption stemming from its bandgap and the swift recombination of charge carriers, have impeded its broader application potential. Encouragingly, these barriers can be mitigated through the modification of TiO₂. In this review, the common synthesis methods of TiO₂ are reviewed, and the research progress of TiO₂ modification technology at home and abroad is discussed in detail, including precious metal deposition, transition metal doping, rare earth metal doping, composite semiconductors, and composite polymers. These modification techniques effectively enhance the absorption capacity of TiO₂ in the visible region and reduce the recombination rate of carriers and electrons, thus significantly improving its photocatalytic performance. Finally, this paper looks forward to the future development direction of TiO₂ photocatalytic materials, including the exploration of new modified materials, in-depth mechanism research, and performance optimization in practical applications, to provide useful references for further research and application of TiO₂ photocatalytic materials.



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Keywords: titanium dioxide; modification; photocatalysis; organic pollutants

1. Introduction

In recent years, acid rain, eutrophication of water bodies, black and smelly water bodies, PM_{2.5} exceeding standards, and other environmental issues have occurred frequently, warning us that environmental protection cannot be delayed. Among them, the content of organic pollutants and pigments is high, which seriously affects the regional water quality [1,2]. Due to their highly stable structure and difficulty in handling, most of them are toxic to organisms, including direct lethality and carcinogenicity [3–5]. This highlights the urgent need for effective treatment of pollutants in water, and the current treatment methods for organic pollutants are mainly the combination of physical, biochemical, and chemical treatment methods [6].

Physical treatment methods include adsorption, extraction, radiation-based techniques, and membrane separation [7–9]. Biochemical treatment methods include aerobic treatment, anaerobic treatment [10,11], and so on. Chemical treatment methods include chemical oxidation, photocatalytic oxidation, electrochemical methods, chemical coagulation, and others [12–14]. Although the traditional physical and chemical treatment methods can remove azo dyes to a certain extent, there are often problems such as high energy consumption, long treatment cycles, and secondary pollution. Therefore, the development of efficient and environmentally friendly treatment of water pollutants has become the focus of current research.

As a new type of wastewater treatment technology being gradually developed based on photochemical oxidation [15], photocatalytic technology has garnered widespread favor among scholars due to its numerous advantages including good stability, high activity, non-toxicity, a wide range of applicability, and the absence of secondary pollution. Its ability to effectively degrade dye pollutants in water bodies is particularly noteworthy [16,17]. Photocatalysts are primarily composed of n-type semiconductor materials, including TiO_2 , ZnO , CdS , and others. TiO_2 stands out as the most extensively studied and utilized n-type semiconductor material due to its exceptional chemical stability, non-toxicity, low cost, and strong photosensitivity [18,19]. Its application areas span water treatment, air purification, solar cell photosensitizers, self-cleaning materials, and medical applications [20]. In the degradation of organic pollutants in water, TiO_2 photocatalysis technology has shown unique advantages. TiO_2 photocatalyst can generate photogenerated electrons and holes under ultraviolet irradiation and then trigger a series of REDOX reactions. These reactions can break the chemical bonds of organic pollutant molecules and degrade them into small molecular compounds, ultimately achieving the purpose of removing the pollutants [21].

Although TiO_2 photocatalysis technology has many advantages in the degradation of pollutants in water, pure TiO_2 , with a band gap of 3.0~3.2 eV [22], can only be excited by ultraviolet light with a wavelength less than 387 nm and photogenerated electron-hole pairs are easy to recombine, resulting in low photo quantum efficiency and limited photocatalytic activity [23]. To further improve the photocatalytic performance of TiO_2 , researchers modified TiO_2 through doping [24], composite, surface modification [25], and other means to optimize the structure of TiO_2 , thereby expanding its photoresponse range and reducing the carrier recombination rate [26,27]. Thus, its application effect in the photodegradation of organic pollutants was enhanced. These modification methods can significantly improve the efficiency and performance of TiO_2 photocatalysts in degrading pollutants and provide better technical support for practical applications. In addition, the study of TiO_2 -modified photocatalysis technology has far-reaching significance [28]. It not only helps to solve the environmental problems of organic pollutants such as azo dyes but also promotes the application and development of photocatalysis technology in other fields [29]. Through in-depth research on the mechanism and methods of TiO_2 modification, theoretical guidance, and practical experience can be provided for the development of more efficient and environmentally friendly photocatalytic materials and contribute to environmental protection and sustainable development [30].

2. Mechanism and Kinetics of Photodegradation of Organic Pollutants by TiO_2 Photocatalyst

2.1. Mechanism of Photodegradation of Organic Pollutants by TiO_2 Photocatalyst

TiO_2 is a semiconductor, and its band structure is composed of a low-level valence band and a high-level conduction band [31]. The valence band is mainly composed of 2p orbitals of oxygen atoms, and the conduction band is mainly composed of 3d, 4s, and 4p orbitals of titanium atoms [32]. The band discontinuity of the semiconductor is bandgap between the valence band and the conduction band, and the energy difference between the conduction band and the valence band is called bandgap width [33].

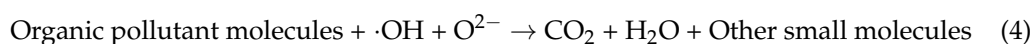
TiO_2 mainly has three crystal structures, namely Anatase type, Rutile type, and Brookite type, of which rutile TiO_2 is the most stable crystal type, even at high temperatures will not be transformed and decomposed. The photocatalytic activity of anatase TiO_2 is higher than that of rutile TiO_2 because anatase TiO_2 has a lighter effective mass, smaller particle size, and longer life of photoexcited electrons and holes [34]. As a metastable phase, titanite is rarely found in nature, is difficult to synthesize, and has low practical application value, so anatase-type TiO_2 is often used to photocatalyze the degradation of organic pollutants in water. For anatase phase TiO_2 , when it is irradiated by photons with energy greater than 3.2 eV (wavelength < 387.5 nm), the photoexcitation reaction will produce free electrons and holes:



Excited electrons react with oxygen in the air to produce superoxide radical anions, which combine with water molecules to form hydroxyl radicals:



Hydroxyl radicals and superoxide radicals with strong oxidation react with organic pollutants, destroying their molecular structure; they are easily broken by oxidation. After a series of reactions, organic pollutant molecules are decomposed into harmless small molecules or low-toxicity compounds, such as water and carbon dioxide. The process is as follows:



The photocatalytic mechanism of TiO_2 is depicted in Figure 1.

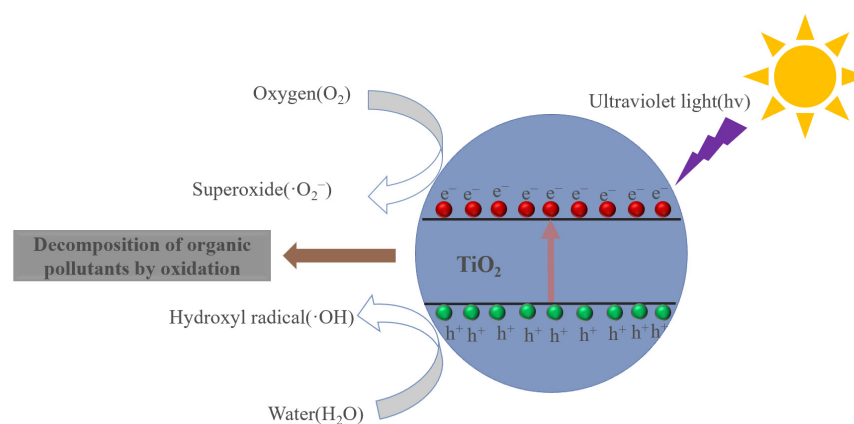


Figure 1. Photocatalytic mechanism of TiO_2 .

2.2. Kinetics of Photodegradation of Organic Pollutants by TiO_2 Photocatalyst

The photocatalytic degradation of organic pollutants by TiO_2 is analyzed by the Langmuir–Hinshelwood model [35]; Arikal [36] et al. used chitosan as a carrier to immobilize TiO_2 /MgO nanocomposites on chitosan beads. MO and azo red S (ARS) were used as model dye compounds. The experimental results showed that the degradation of the pollutants followed first-order kinetics, and the Langmuir–Hinshelwood model was suitable for describing the kinetics of the photocatalytic degradation of wastewater. This is simplified as the first-order kinetics formula: $\ln(C_0/C) = kt$, (C_0) the initial concentration of organic pollutants, (C) the concentration of organic pollutants after degradation, (k) the apparent reaction rate constant, and (t) the photodegradation time. The model takes into account the adsorption and reaction processes on the catalyst surface and can describe the kinetic behavior of photocatalytic degradation well. The kinetics of photocatalytic degradation can be described by the degradation rate constant. The degradation rate constant reflects the relationship between degradation rate and pollutant concentration.

The influencing factors of reaction kinetics are as follows:

- Solution pH value has an important effect on photocatalytic degradation. The photocatalytic activity of TiO_2 may vary under acidic and alkaline conditions.
- The amount of catalyst dosing will also affect the degradation rate. Less than or more than the optimal dosage will lead to a decrease in the degradation rate.
- Factors such as organic pollutant's initial concentration and light intensity also affect the kinetic process of photocatalytic degradation.

In summary, the process of photodegradation of organic pollutants using TiO_2 photocatalyst involves complex chemical reactions and kinetic behaviors. Through an in-depth

understanding of its mechanism and kinetics, the photocatalytic degradation process can be optimized, and the degradation efficiency and environmental protection effect can be improved.

3. Synthesis Method of TiO₂ Photocatalyst

As a functional material, TiO₂ has high photocatalytic activity and, therefore, has an excellent advantage in the field of photocatalytic degradation. At present, the methods commonly used to synthesize TiO₂ include the sol-gel method, hydrothermal method, atomic layer deposition method, and microemulsion method. In terms of structure and morphology, a variety of morphologically controllable TiO₂ micro-nano meters, such as nanorods, nanotubes, nano-flowers, nano-hollow spheres, and mesoporous structures, were prepared through various experiments. As shown in Figure 2, these micro-nano TiO₂ materials with large specific surface areas usually have more excellent photocatalytic properties.

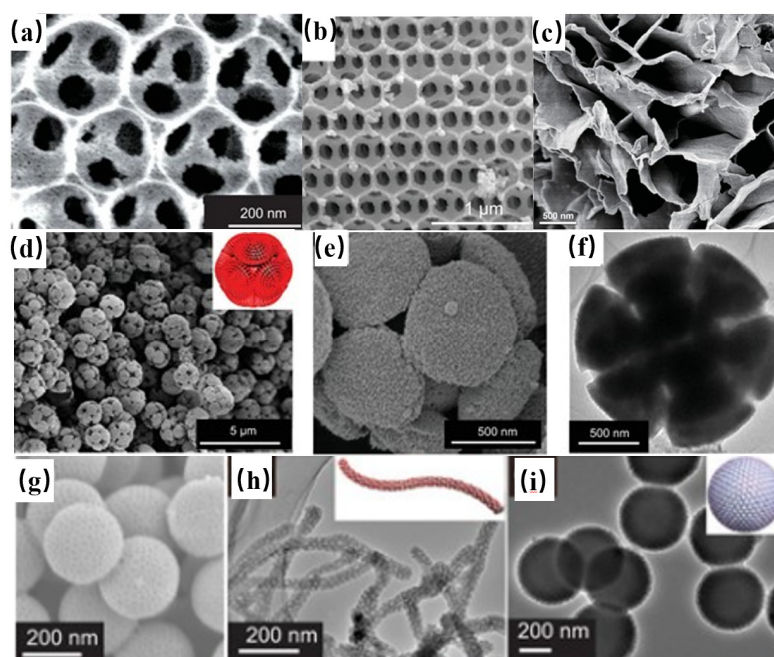


Figure 2. Different TiO₂ micro-nano structure diagram: (a) SEM image of ordered macroporous TiO₂; (b) Porous TiO₂ TEM image; (c) TEM image; TiO₂ flower-like superstructure self-assembled by limiting microemulsions. FESEM (d,e) and TEM (f) images of primary mesoporous TiO₂; (g) SiO₂ monolayer mesoporous TiO₂ core-shell structure; (h) Carbon nanotube-coated TiO₂ TEM and FESEM images; (i) carbon cluster TiO₂ TEM image [37].

3.1. Sol-Gel Method

Sol-gel is the most commonly used process method for preparing TiO₂ photocatalytic materials [38]. Inorganic salts and Alkoxides (including tetraethyl titanate, butyl titanate, isopropanol titanium, etc.) are placed in distilled water, mixed evenly at room temperature under liquid phase conditions, and a stable, transparent sol system is formed in solution through chemical reaction steps such as hydrolysis and condensation, as shown in Figure 3. After aging for some time, the colloidal gel slowly polymerizes to form a wet gel with a three-dimensional network structure, and the gel network is filled with solvent that loses fluidity. The wet gel is prepared by vacuum drying, high-temperature roasting, and curing to produce molecular and even nanostructured materials. Nanomaterials prepared by the sol-gel method have the advantages of high purity, uniformity, and controllable morphology and have been widely used in the preparation of TiO₂.

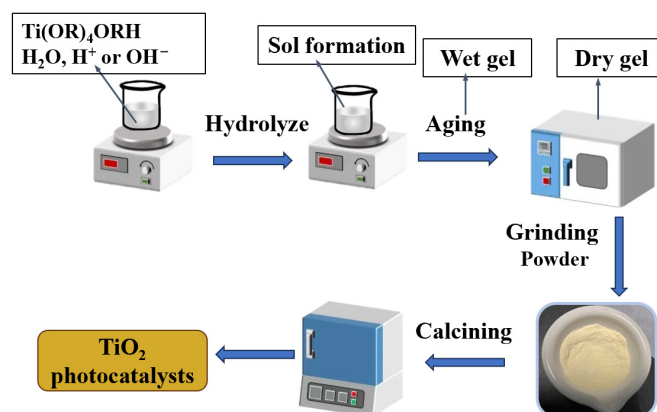


Figure 3. Schematic diagram of TiO_2 preparation process by sol-gel method.

Jamil [39], Huo [40], Fermeli [41], et al. prepared a composite photocatalyst by sol-gel method. The results show that the prepared TiO_2 composite photocatalyst has good dispersibility, a large specific surface area, and good photocatalytic activity. Dinkar Parashar [42] prepared photocatalysts by sol-gel method at different calcination temperatures (400–800 °C) and hydroalcohol ratios. The activity of TiO_2 prepared by the sol-gel method was higher than that of commercially available pure anatase TiO_2 nanoparticles due to the smaller average particle size. It was found that the ratio of water to alcohol in the preparation of TiO_2 catalysts had a significant effect on antibiotic removal. Namely, the removal-rate constants of metronidazole (MNZ), ciprofloxacin (CIP), and tetracycline (TET) were improved by a factor of 2.7, 3.3, and 1.6, which further indicates that the sol-gel prepared TiO_2 can effectively remove the harmful substance. Lalitha [43] et al. synthesized TiO_2/ZnO with quadrilateral and hexagonal structures by sol-gel method; the catalyst displayed 90% degradation within 40 min under UV light conditions.

3.2. Hydrothermal Synthesis

The hydrothermal synthesis method is a reaction occurring at high temperature and high pressure [44], which uses water or organic solvent as a medium through heating so that insoluble or insoluble substances are dissolved or recrystallized after washing and centrifugation to obtain the required nanoparticle. Rawat [45], Matakane [46], et al. prepared composite photocatalysts by hydrothermal method. The results of photocatalytic performance show that it has good absorption ability to ultraviolet light and good transmittability to visible light. Yang [47] et al. synthesized a novel 3D sea urchin-type titanium dioxide by the EDTA- Na_2 -assisted hydrothermal method (Figure 4). Benefiting from the conical structure prepared by the hydrothermal method and the rapid separation of photogenerated electron holes in the mixed crystal phase, the sub-micron-sized 3D sea urchin-type titanium dioxide can efficiently degrade 94.1% of the methicillin in the aqueous solution in 90 min, which is superior to that of the commercially available 25 nm-sized rutile titanium dioxide. Zhang [48] et al. modified TiO_2 with a carboxyl group and amino group by hydrothermal method, making the adsorption performance of functionalized TiO_2 better than P25 (unmodified commercial TiO_2). Moreover, the functionalized TiO_2 has good reusability for the removal of azo dye acid red G even after 5 adsorption–desorption cycles.

With the progress of scientific research, the hydrothermal method has attracted more and more attention from researchers, especially hydrothermal crystal growth, which has become the focus of research and will become the development object of the scientific research community. Hydrothermal preparation of nanomaterials equipment and conditions still need to be further explored and studied.

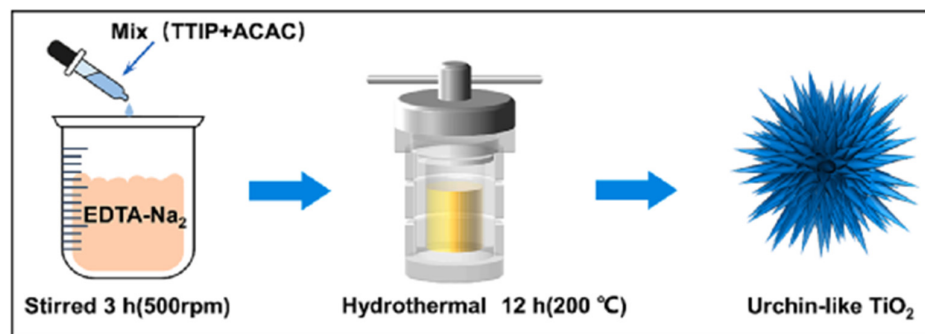


Figure 4. Preparation process of sea urchin-type titanium dioxide [47].

3.3. Atomic Layer Deposition Method

Atomic layer deposition (ALD) technology, also known as Atomic layer epitaxy (ALE) technology, is a chemical vapor deposition technology based on ordered surface autosaturation reactions. Generally speaking, it is a method of coating the material layer by layer on the substrate surface in the form of a single atomic film. Jialin [49], Abidi [50], et al. used the atomic deposition method to prepare TiO_2 and found that the prepared TiO_2 nanoparticles were still anatase-type at high temperatures, had particularly good dispersion, and had high photocatalytic activity after degrading dyes. Cao [51] et al. modified the ultra-thin Fe_2O_3 layer of industrial anatase TiO_2 powder by atomic layer deposition (ALD). The ultra-thin Fe_2O_3 coating with a small band gap of 2.20 eV can increase the visible light absorption of the TiO_2 carrier, and the degradation efficiency of TiO_2 powder coated with ALD Fe_2O_3 is the highest within 90 min, reaching 97.4%. Feng [52] et al. used atomic layer deposition (ALD) to deposit TiO_2 nanoparticles on carbon nanotube membranes to prepare hydrophilic electrodes, as shown in Figure 5. After 20 ALD cycles, the modified carbon nanotube membranes showed better electrosorption performance and reusability in the CDI process. The total Cr and Cr(VI) removal significantly increased to 92.1% and 93.3%, respectively. This work demonstrates that ALD is a highly controllable and simple method for the preparation of advanced CDI electrodes, broadening the application of metal oxide/carbon composites in electrochemical processes, especially in the field of photocatalytic degradation of organic pollutants.

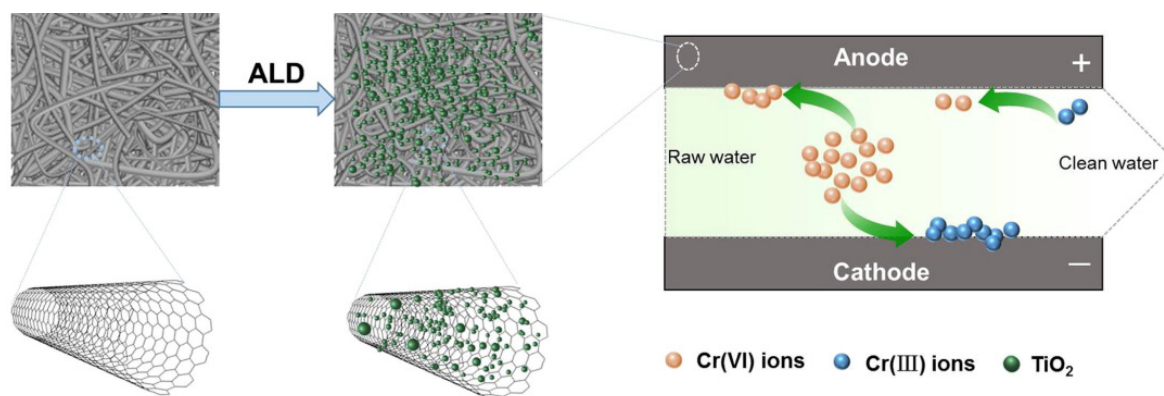


Figure 5. Atomic layer deposition (ALD) deposition of TiO_2 nanoparticles on carbon nanotube film [52].

Furthermore, Ostyn et al. [53] prepared TiO_2 film on graphene with ALD and oxidized the surface of graphite. The film has a high UV transmittance of 95%, which simplifies the experimental design. No chemical reagents are used to reduce the risk of contamination. TiO_2 films prepared by ALD react rapidly in graphite photooxidation, which is superior to traditional powder photocatalysts. Ke et al. [54] grew TiO_2 films by depositing atomic layers on silica support (SBA-15) and depositing precious metal Au on them and found

that titanium dioxide films can successfully grow on mesoporous materials, increasing the specific surface area of the catalyst. Lys et al. [55] successfully combined laser-induced Si nano-fringes (SiNR), MXene, and TiO_2 to produce efficient ternary photocatalytic materials through ALD technology. Experiments show that the material has strong absorption capacity in the spectrum range, high stability, repeatability, and photocatalytic efficiency, which provides a new way for the photodegradation of azo dyes in wastewater treatment and shows broad application prospects.

3.4. Microemulsion Method

The microemulsion method is used for the preparation of nano or polymeric materials by adding surfactants and co-solvents and mixing the immiscible solution into a homogeneous phase [56]. Its advantage is that it can prepare nano-sized and highly dispersible materials with mild conditions and high-quality performance. Because of the large interfacial area and high surface activity of microemulsion, it can improve the reaction efficiency and yield, which is widely used in the preparation of nanomaterials, polymer materials, and catalysts.

Sun [57] et al. prepared $\text{Fe}_3\text{O}_4/\text{TiO}_2$ composite photocatalyst by microemulsion-solvothermal method. It was found that $\text{Fe}_3\text{O}_4/\text{TiO}_2$ could reduce the band gap, and the degradation rates of $\text{Fe}_3\text{O}_4/\text{TiO}_2$ and TiO_2 for acid red 73 were 93.56% and 74.47%, respectively. Yang [58] et al. successfully prepared TiO_2 nanofibers with porous and mixed-crystal structures by the microemulsion method, which can directly regulate the structure of titanium dioxide nanofibers by changing the microemulsion system. The titanium dioxide obtained by the microemulsion method shows a porous and mixed-crystal structure and excellent photocatalytic properties. It is simple to prepare and is of great importance for the application of the preparation and enhancement of the performance of the special-shape photocatalytic materials. The degradation rate of methylene blue solution was as high as 98% after 90 min, which was effective in the treatment of printing and dyeing wastewater.

However, the microemulsion method also has limitations that include the following: the product purity is not high, the reagent is difficult to completely remove, the precursor must be water-soluble or oil-soluble, and the preparation and control of the microemulsion is complicated, which requires experimental experience and technical skill.

3.5. Other Synthesis Methods

In addition to the above four most common methods for synthesizing TiO_2 , there is also the Suzuki coupling reaction method [59], the electrostatic spinning method [60], the one-pot method [61], etc. Suzuki coupling reaction is a palladium-catalyzed cross-coupling reaction of aryl or alkenyl boronic acids or boronic esters with chlorine, bromine, iodine-substituted aromatic hydrocarbons or olefins. The one-pot method is a method in which the reactants are made to undergo successive multi-step reactions in a single reactor to improve the reaction efficiency. TiO_2 preparation by electrostatic spinning is a method of stretching titanium-containing solution into fibers using a high-voltage electric field, followed by heat treatment to obtain TiO_2 nanofibers. Djeda [62] et al. prepared layered double hydroxide (LDH)/ TiO_2 nanocomposites with photocatalytic properties by immersion and direct coprecipitation methods and compared them with pure TiO_2 colloidal solutions. The degradation experiments showed that MgAl LDH/ TiO_2 prepared by the coprecipitation method had the highest photodegradation efficiency for Orange II, which emphasized the importance of the preparation method of nanocomposites. Suitable synthesis methods can be selected according to different application requirements.

In summary, the most commonly used synthesis methods of TiO_2 photocatalysts, their reaction principles, and their advantages and disadvantages are shown in Table 1.

Table 1. Reaction Principle of TiO₂ Photocatalyst Common Preparation Methods and Their Advantages and Disadvantages.

Preparation Methods	Reaction Principle	Advantages	Disadvantages
sol-gel method	Inorganic salts and alcohol salts are hydrolyzed in distilled water, polymerized into a gel after hydrolysis, dried in a vacuum, and cured by high-temperature calcination.	Good dispersion; easy to control the reaction; simple process; low cost and cost-effective.	Long preparation time; many operating steps.
hydrothermal synthesis	In a closed system, using water as a solvent, the mixture reacts under certain temperature conditions.	Mild reaction conditions; high purity, good dispersion, crystalline form, controllable shape; environmentally friendly.	High equipment requirements; technically difficult and costly.
atomic layer deposition	A chemical vapor phase thin film deposition technique in which a substance is deposited on the surface of a substrate layer by layer in a single-atom-film format.	High accuracy; high atom utilization.	Expensive equipment; cumbersome process; difficult to promote industrialization.
microemulsion method	Mutually incompatible liquids form microreactors in the presence of surfactants for the preparation of nanomaterials.	Good dispersion of prepared samples; mild conditions; improved precursor reaction rate.	Poor purity; precursors may not be soluble; complex preparation.

Combined with the advantages and disadvantages of the four preparation methods—the sol-gel method, hydrothermal method, microemulsion method, and atomic deposition method—the improvement measures of TiO₂ preparation in the future can be focused on improving the preparation efficiency, reducing the cost, optimizing the performance, and meeting specific application needs. Through the above different preparation methods, two or more preparation methods can be combined according to the need to prepare the new, more stable, and higher photocatalytic efficiency of terpolymer or multi-component modified TiO₂ photocatalytic materials.

4. Modification Method of TiO₂ Photocatalyst

The direct preparation of TiO₂ sols can effectively solve the application challenges of TiO₂ particles, such as easy agglomeration and difficult loading [63]. However, TiO₂ nanocrystals in sol still face the problems of limited photoresponse range and high carrier complexation rate. To further enhance its photocatalytic performance, it is necessary to broaden the light absorption range of TiO₂ nanocrystalline sols and improve the separation efficiency of their photogenerated carriers by various modification methods.

4.1. Precious Metal-Doped Titanium Dioxide

Precious metals and TiO₂ have different Fermi energy levels, and the work function of the metal is higher than that of the semiconductor TiO₂; electrons usually tend to flow from the semiconductor to the metal when the two are in contact [64]. This cross-interface migration of electrons contributes to the efficient separation of electrons and holes in the semiconductor, as shown in Figure 6. Therefore, noble metals such as gold (Au), silver (Ag), platinum (Pt), and palladium (Pd) can significantly enhance the photocatalytic activity of TiO₂ materials [65]. In these applications, noble metal nanoparticles play a key role in trapping or transferring photogenerated electrons [66].

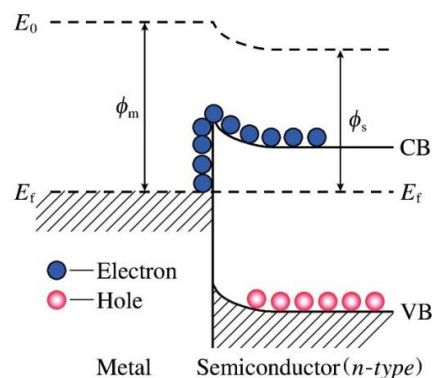


Figure 6. Schematic diagram of electron transfer in the noble metal deposition system [67].

The precious metal silver is relatively cheap and readily available [68]. Several studies, such as Chacon-Argaez [69], Borrego Pérez [70], etc., have found that the photocatalytic activity of composites is indeed significantly improved. Mohammed, W [71] et al. found that Schottky promoted electron transfer at Ag-TiO₂, transferred the absorption to the visible region, reduced the band gap of TiO₂, and inhibited electron-hole recombination, thus enhancing the photocatalytic activity and stability.

Other precious metal deposits, such as Wang et al. [72] promoted the interaction between Pt and TiO₂ by introducing oxygen vacancies through the carrier material, which facilitated the charge transfer from the carrier to Pt and exhibited excellent redox properties. Liu et al. [73] successfully prepared Au-TiO₂ nanoparticles by the hydrothermal synthesis method and found that the optical band gap value of the composites decreased due to the doping of Au or the formation of oxygen vacancies, etc., which induced a narrowing of the Au-TiO₂ band gap and increased visible light absorption, thus effectively degrading the MB.

The noble metal nanoparticles have a high specific surface area, good surface activity, and small particle size, which are characteristic of multiphase catalysis [74,75]. However, the catalytic activity may be limited by the limited ability of noble metals to absorb light at specific wavelengths [76,77]. In addition, the precious metal deposited TiO₂ is less efficient in utilizing visible light and requires higher energy of UV light for better catalytic effect. However, precious metals are expensive resources, and doping them into TiO₂ also increases the processing cost, which may be less economical in large-scale applications.

4.2. Transition Metal-Doped Titanium Dioxide

Interestingly, doping a moderate amount of transition metal ions in TiO₂, the electrons in the d- and f-orbitals can undergo a transition and enter into the TiO₂ structure, which reduces the bandgap and shifts the absorption edge to the visible region and reduces the rate of carrier complexation, thus improving the photocatalytic efficiency of TiO₂ [78]. At present, the transition metal doped ions are applied more: iron (Fe³⁺), copper (Cu²⁺), manganese (Mn²⁺), vanadium (V⁴⁺), zinc (Zn²⁺), etc [79].

4.2.1. Doping with a Single Transition Metal Elements

When TiO₂ is doped with a single transition metal ion, the addition of the transition metal elements will change the lattice structure of TiO₂ and thus its crystal crystallinity since they have multiple valences. This change affects the compounding process of photogenerated electrons and holes, thus improving the photocatalytic activity. Meshram et al. [80] microwave synthesized TiO₂-Al composite photocatalysts and found that the surface area and porosity of the composites were significantly reduced compared to their pristine components and were successfully used for the degradation of mixed azodyes such as methylene blue and rhodamine B. Zhu et al. [81] prepared iron-doped TiO₂ thin films, and concluded that the right amount of iron ions effectively inhibited the composite to enhance the photogeneration of the rate of electron holes and that the enhanced photoactivity of

Fe-doped TiO_2 samples was due to the generation of new elements to generate electronic states within the TiO_2 band gap. Mingmongkol et al. [82] prepared TiO_2 -doped composite photocatalysts with transition metal Cu and found that Cu doping did not cause any difference in the particle size or specific surface area, and on the other hand, the surface of the TiO_2 material doped with high concentration of Cu charge transfer had a negative effect. Cu-doped TiO_2 showed much greater photocatalytic degradation of methylene blue compared to undoped TiO_2 .

4.2.2. Co-Doping of Transition Metal Elements

In contrast, co-doping transition metals may produce more complex effects. Co-doping implies the simultaneous introduction of two or more different transition metal ions into TiO_2 . Co-doping may further enhance the efficiency of photogenerated electron-hole separation through synergistic effects or broaden the light absorption range of TiO_2 by introducing new energy levels. Rao et al. [83] prepared Cu and Zn co-doped TiO_2 nano-photocatalysts and found that the addition of Cu and Zn to TiO_2 hindered the growth of nanoparticles, and there existed a more efficient electron-hole generation. Sukhadeve et al. [84] prepared Zn and Fe co-doped TiO_2 nanoparticles using a simple sol-gel process, and the absorption spectra of the prepared nanoparticles showed strong absorption in visible light. The synergistic effect produced by Zn and Fe blocked the photoinduced charge carriers and delayed the complexation probability, which greatly improved the RhB, MG, and MB mixture pollution degradation efficiency.

Transition metal elements have multiple valence, which can promote the chemical reaction in the electronic conduction of TiO_2 , but it is worth noting that the doping amount should be controlled. Otherwise, it is not conducive to the improvement of the catalytic performance, and dopants are prone to agglomeration [85], such as the surface of the enriched or even the formation of new phases, so that the effective surface area of the semiconductor material is reduced, resulting in a decrease in the activity [86].

4.3. Rare Earth Metal-Doped Titanium Dioxide

Due to their unique electronic orbital structure [87], the doping of rare earth metal ions can adjust the energy level structure of TiO_2 , enabling it to absorb more light within the visible light range and thus enhancing photocatalytic activity [88]. Additionally, rare earth metal doping can introduce additional energy levels, promoting the separation of photogenerated electrons and holes [89]. It can also improve the photostability of titanium dioxide, enhancing its long-term stability and extending the lifespan of photocatalytic materials [90]. This opens up new possibilities for its application in environmental purification, water treatment, energy conversion, and other fields [91]. Common rare earth metals used for doping include yttrium, erbium, holmium, lan, cerium, yttrium, and europium [92].

4.3.1. Doping with a Single Rare Earth Metal Element

Single rare earth element doped TiO_2 is relatively easy to synthesize and can be more easily achieved in the TiO_2 lattice for control and regulation [93]. Ćurković et al. [94] prepared Ce doped TiO_2 nanocomposites by sol-gel method and found that the absorption of the composites in the visible light band was higher than that of pure TiO_2 nanomaterials, and three cycles could be reused. Ikram Benammar et al. [95] used a hydrothermal-assisted sol-gel method to prepare rare earth yttrium and erbium-doped TiO_2 , respectively, and the optical properties were improved after heat treatment of the powders and down-conversion of erbium-doped nanoparticles was observed.

4.3.2. Co-Doping with Rare Earth Metal Elements

Single transition metal element doping may not be able to fully optimize the energy band structure of TiO_2 [96], while rare earth element co-doping can extend the light absorption range of TiO_2 , enabling it to absorb wider wavelength bands of light [97],

enhancing the light absorption capacity and photoelectric conversion efficiency of TiO_2 , and improving the stability of the catalyst surface [98].

Pascariu [99] et al. used electrospinning calcination of normal TiO_2 doped with Sm^{3+} and Er^{3+} to demonstrate the stability and reusability of the catalyst in five repeated cycles of photodegradation of MB. Guetni et al. [100] designed a new co-doped TiO_2 with Nd-Sm and La/Y apatite nanoparticles, which showed the highest degradation rate of 96.49% for azo dye Orange Yellow G within 105 min. Ren et al. [101] used the classical sol-gel method to prepare TiO_2 nanoparticles co-doped with rare earth elements Ce and Er, as shown in Figure 7. The composite photocatalyst is a spherical particle with an uneven radius. It can be seen in Figure 7c that the polyhedral structure is mainly composed of hexagons and rhomboids, with an average size of 30 nm. The results show that Ce doping can reduce the band gap width of the composite and give it the ability to respond to visible light. At the same time, the upconversion luminescence characteristics of Er can convert near-infrared light in the solar spectrum into short-wave light that is more easily absorbed by TiO_2 , thus enhancing the utilization rate of sunlight by the material. In addition, the doping of these two rare earth elements can effectively promote the separation and migration of photogenerated electrons and holes and optimize carrier utilization efficiency. Therefore, doped TiO_2 nanoparticles show better photocatalytic performance.

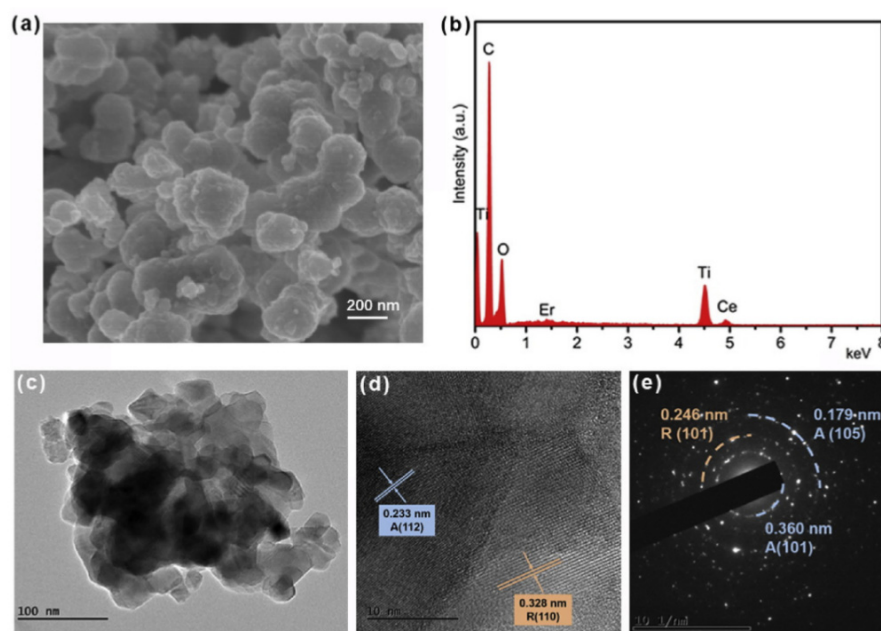


Figure 7. Characterizations of the $\text{Er}_{0.5}\text{Ce}_{0.2}\text{Ti-O}$: (a) SEM image; (b) EDS spectrum; (c) TEM image; (d) High-resolution TEM image; (e) selected area electron diffraction (SAED) pattern [101].

4.3.3. Co-Doping of Rare Earth Elements with Other Elements

Co-doping of rare earth elements with other elements has also attracted extensive research [102,103]. Li Jia et al. [104] synthesized lanthanum, graphene oxide (GO), and TiO_2 by sol-gel method to prepare an efficient photocatalytic material with visible light response. Lattice distortion occurred in the samples added with the rare earth element lanthanum, which increased the surface area of the photocatalyst and significantly improved the photocatalytic activity of TiO_2 . The degradation efficiency of acid red B reached 95.6% after 5 h of simulated sunlight irradiation.

Co-doping of rare earth elements with other elements increases the separation efficiency of photogenerated electron-hole pairs and the number of surface active sites and improves the utilization efficiency of visible and infrared light. However, the co-doping of rare earth elements with other elements involves the synthesis and control of multi-element systems, so the preparation process and conditions are more complicated [105,106].

4.4. Compound Semiconductors Based on Titanium Dioxide

Semiconductor compounding is a method used to enhance photocatalytic efficiency by combining different types of semiconductor materials to form heterojunctions, as exemplified in Figure 8, which depicts a p-n heterojunction formed by TiO_2 and ZnO . The semiconductor composite effectively improves photocatalytic efficiency due to the following advantages:

1. By manipulating the size of the modified particles, the spectral absorption range and bandgap of the semiconductor material can be effectively tuned utilizing the quantum size effect [107,108].
2. Surface modification of TiO_2 plays a role in improving the photostability of the semiconductor materials [109].
3. Given that light absorption in semiconductors mainly occurs at the band-edge, the semiconductor composite facilitates more efficient harvesting of sunlight [110].

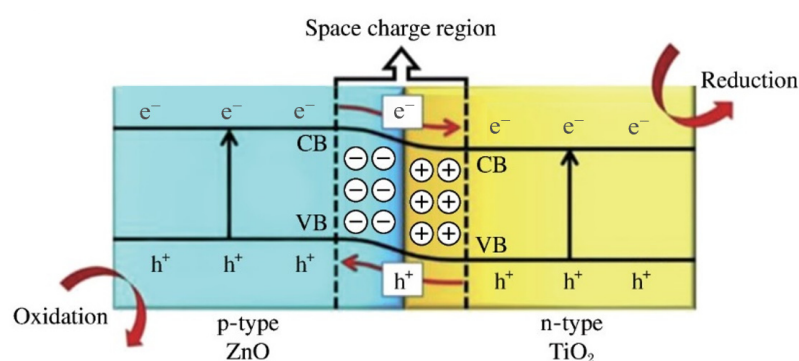


Figure 8. Schematic diagram of p-n junction formation between TiO_2 and ZnO [110].

4.4.1. Titanium Dioxide Composites with Common Semiconductors

Wongburapachart [111] et al. prepared $\text{TiO}_2/\text{NiO-TiO}_2$ bilayer film photocatalyst (BLF) for photocatalytic degradation measurement using acid orange 7 (AO7) solution under light and dark conditions. It was found that compared with ordinary TiO_2 , the photocatalytic activity of the prepared sample was increased by about 8 times after 48 h of AO7 degradation. Bai [112] et al. synthesized TiO_2/ZnO composites by the sol-gel method and the hydrothermal method and found that they have obvious heterostructures, which can reduce the band gap width and improve the light absorption intensity. The photocatalytic mechanism is shown in Figure 9. Ratanathavorn Wittawat et al. [113] prepared TiO_2/ZnO composite spherical particles. TiO_2/ZnO composite also showed much higher catalytic activity compared to a single component. In addition, Wang et al. [114] also prepared ZnO-TiO_2 materials with different composite ratios and found that the specific surface area, pore volume, and pore diameter of ZnO-TiO_2 composites were significantly larger than those of TiO_2 and the ZnO-TiO_2 composites were more surface acidic. The energy band structure facilitates the efficient separation of electrons and holes, and the catalytic reduction activity and selectivity are stronger. It is further shown that TiO_2 composite with ZnO can inhibit TiO_2 crystal transition and particle growth, and the UV absorption ability is enhanced [115]. Abumousa [116] et al. prepared ternary $\text{TiO}_2/\text{Y}_2\text{O}_3/\text{g-C}_3\text{N}_4$ nanocomposites by a simple sonochemical method, which showed excellent photocatalytic properties in the degradation of Congo red dye, Malachite green, and other dyes in aqueous solutions in a short time. These binary semiconductor composites and ternary composites are based on TiO_2 to form heterostructures, and the interface effect and energy band migration in the heterostructures can promote the transfer of photogenerated electrons and holes, thereby improving the rate and efficiency of the photocatalytic reaction.

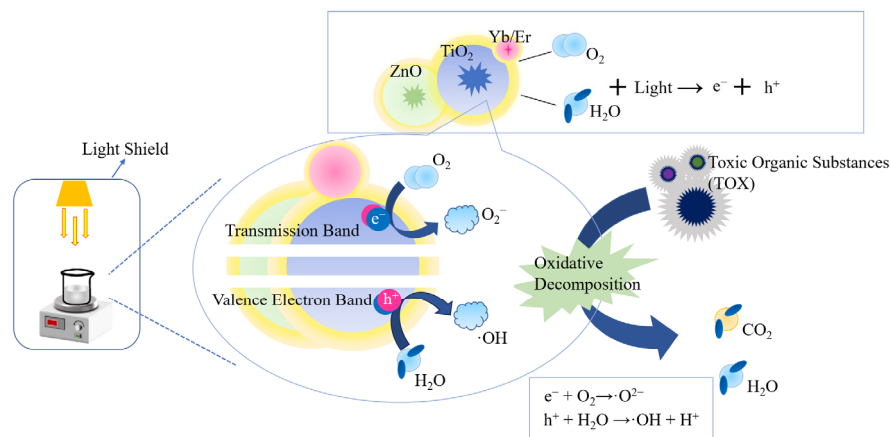


Figure 9. Proposed schematic diagram of the TiO₂/ZnO photocatalyst.

TiO₂ is composited with other semiconductors to form a composite semiconductor material. This new composite material broadens the excitation wavelengths available to the catalyst, effectively regulates the performance of individual materials, and generates numerous novel photochemical and photophysical properties. In recent years, numerous studies have been conducted on binary semiconductor composites, such as TiO₂/ZnO, TiO₂/CdS, TiO₂/WO₃, and ZnO/ZnS, among others. The photocatalytic performance of these compound semiconductors surpasses that of a single semiconductor.

4.4.2. Titanium Dioxide Hybrid Materials with Graphene

In recent years, the modification of graphene composite TiO₂ has become the focus of many researchers. Graphene with a two-dimensional structure has a large number of two-dimensional conjugated structures, so people combine graphene with TiO₂ to enhance the photocatalytic performance of TiO₂, which has been extensively studied in this area. Heltina [117], Wang [118], and others prepared TiO₂ with different graphene (GO) composite ratios compared to the pure TiO₂ and the composite TiO₂/GO catalysts. The smaller grain size and higher adsorbed oxygen/lattice oxygen ratio exhibited superior photocatalytic performance. In addition, GO acts as a capture center for photogenerated electrons and transfers electrons to the target reactants, thus inhibiting the recombination rate of photogenerated electron-hole pairs and increasing the photocatalytic rate of TiO₂.

However, graphene tends to aggregate in solution to form clusters, which can lead to difficulties in controlling the homogeneity and dispersion of graphene in the composites [119], and the preparation of composites of titanium dioxide and graphene usually requires special synthesis techniques and equipment, which may lead to high preparation costs. This makes these composites difficult to commercialize on a large scale for some applications.

4.5. TiO₂ Composite Polymers

Combining modified TiO₂ with polymers can endow nanocomposite materials with new properties. Additionally, polymers can enhance the adsorption and photocatalytic performance of nano-TiO₂, facilitating its separation and recovery [120].

Maeda et al. [121] first employed a phosphorus coupling agent to modify the surface of the modified TiO₂ particles, aiming to enhance their compatibility with specific organic monomers (Figure 10). TiO₂@PMMA hybrids were successfully obtained through in situ polymerization. It can be observed that as the in situ polymerization time elongates, the PMMA polymer chains growing on the surface of TiO₂ particles lead to an increase in the distance between the nanoparticles, thereby enhancing the transparency of the PMMA composites. This method maintains the flexibility, film forming, and electrical conductivity of the polymer. In addition, the composite may also exhibit better photocatalytic activity and antimicrobial properties.

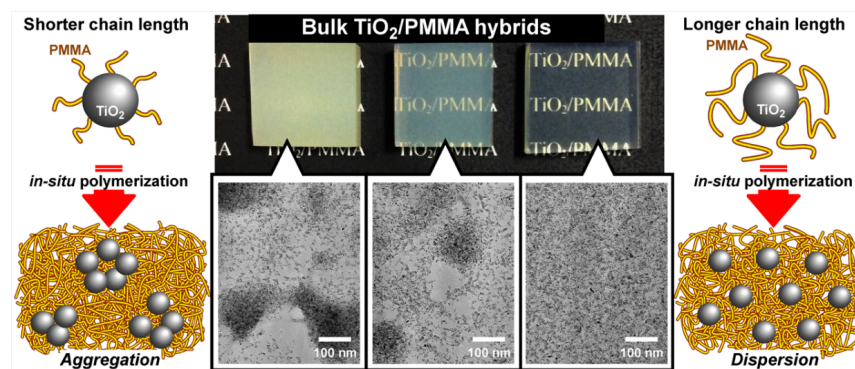


Figure 10. Appearance and TEM image of TiO_2 /PMMA hybrid plate at different polymerization times [121].

Interestingly, Shi et al. [122] first coated stearic acid on the surface of TiO_2 particles by impregnation method and then further modified it with paraffin wax to prepare TiO_2 with Janus structure, which enhances the surface charge separation efficiency and adsorption capacity of organic matter (Figure 11). In addition, the modified Janus-like TiO_2 can be used as an additive to stabilize Pickering emulsion, which in turn enhances its efficiency in degrading oil-phase pollutants in high-concentration kerosene and nitrobenzene wastewater.

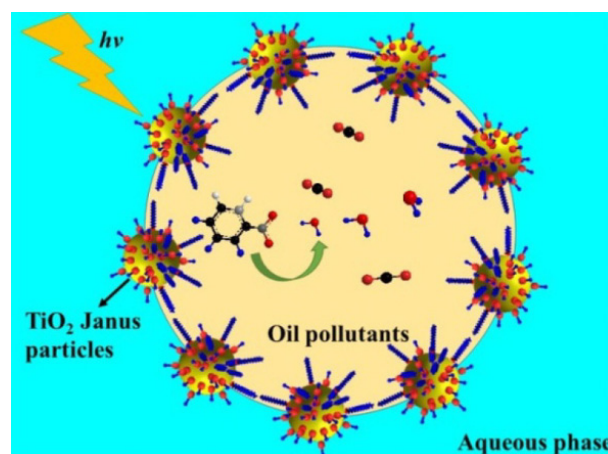


Figure 11. Photocatalytic mechanism diagram of modified TiO_2 /polymer composites [122].

Nair [123] et al. fixed PANI- TiO_2 nanocomposites in polystyrene cubes to form PANI- TiO_2 @polystyrene cubes for photocatalytic degradation of acid yellow 17 (AY 17) dyes under visible light. And the photocatalytic activity was significantly improved. It provides a way to prepare more excellent new photocatalysts. Tran et al. [124] formulated different concentrations of acrylic acid (AA) mixed with isopropanol to modify the nano- TiO_2 and then uniformly coated it on the surface of polyvinylidene fluoride (PVDF) film. At high temperatures, AA reacts with PVDF, and nano- TiO_2 is fixed on the surface of the film to maintain its flexibility and film formation, which can improve the photocatalytic activity of the composite. Neves et al. [125] used polydimethylsiloxane-modified TiO_2 nanoparticles to increase the surface roughness, enhance their hydrophobic strength and photocatalytic activity, and provide ideas for achieving complete degradation of polymers.

5. Summary and Outlook

In recent years, significant progress has been made in the field of TiO_2 modified photodegradation of organic pollutants. Through a series of modification methods, the photocatalytic performance of TiO_2 has been significantly improved, providing a more efficient and reliable solution for the photodegradation process of organic pollutants. The

following is a summary of the research progress in this field in recent years, including prospects of future research development.

5.1. Summary of Research Progress

- By doping precious metals, transition metals, rare earth metals, or non-metallic elements, TiO_2 can change the band structure, broaden its light absorption range, and improve the separation efficiency of photoelectron-hole pairs, which can significantly improve the photocatalytic activity of TiO_2 .
- TiO_2 was mixed with other semiconductor materials to form a composite photocatalytic material with a heterogeneous structure. This modification method can make use of the synergistic effect between different materials to improve the utilization efficiency of photogenerated electron-hole pairs and enhance photocatalytic performance. For example, the composite of TiO_2 with SiO_2 , ZnO , and other materials can form heterogeneous structures and improve photocatalytic efficiency.
- By introducing functional material polymer on the surface of TiO_2 , the surface properties of TiO_2 are improved, and the photocatalytic performance is improved. Surface modification can increase the active sites on the surface of TiO_2 and promote the separation and migration of photogenerated electrons and holes.

The five modification methods mentioned in this paper, the dopants commonly used, the specific surface area, the band gap energy, and degradation effects of the modified TiO_2 photocatalyst are shown in Table 2.

Table 2. Characterization and degradation effect of modified TiO_2 photocatalyst.

Modification Methods of TiO_2	Doping Agents	The Surface Area (Before~After/ $\text{m}^2 \text{ g}^{-1}$)	Bandgap Energy (Before~After/eV)	Catalytic Effect	Reference
Precious Metal-Doped TiO_2	Ag	— —	3.15~2.31	The degradation rate of methylene blue under visible light was 93%.	[126]
	Au	17.8~28.7	3.15~2.9	Methyl orange is completely dissolved within 90 min.	[127]
	Pt	42~68	3.24~2.92	The degradation rate of Dichlo-Rophenoxyacid (2,4-D) was 99%.	[128]
Transition Metal-Doped TiO_2	Fe	— —	3.22~3.20	The removal rate of pollutants reached 97% within 240 min.	[129]
	Mn	50~93.35	3.20~2.21	The degradation rate of pollutants increased from 48.17% to 60.12%.	[130]
	Cu	43~46	3.08~2.78	The reduction rate of organic carbon within 6 h is 75%.	[131]
Rare Earth Metal-Doped TiO_2	La	— —	3.16~3.12	The degradation rate of p-azo dye orange-yellow G was 96.49% in 105 min under UV-VIS spectral radiation.	[100]
	Er	— —	3.15~2.69	The degradation rate of methylene blue was 80% under visible light.	[132]
	Eu	— —	3.43~3.40	The degradation rate of Congo red reached 97%.	[133]
TiO_2 Composites with Common Semiconductors	ZnO	50.05~107.98	3.26~2.76	Under sunlight irradiation, when pH is 5.8, the degradation efficiency of the dye is the highest, which is 92%.	[134]
	SiO_2	217~256	3.22~3.22	At 300 W Xenon lamp irradiation for 60 min, the degradation efficiency of TC is 96%.	[135]
	BiVO_4	60.6~95.3	3.2~3.03	The degradation rate of formaldehyde reached 97.1%.	[136]
	WO_3	95~117	3.0~2.6	Under no light conditions, the degradation rate of pollutants reached 22%.	[137]

Table 2. Cont.

Modification Methods of TiO ₂	Doping Agents	The Surface Area (Before~After/m ² g ^{−1})	Bandgap Energy (Before~After/eV)	Catalytic Effect	Reference
TiO ₂ composite polymers	Triformyl chlorine-melamine polymer (TMP)	13~17	3.78~2.82	It can degrade 96.1% RhB.	[138]
	Polyaniline titanium Dioxide quantum Dots (PAN-TiQD)	— —	2.95~2.82	The degradation rate of Dianix blue dye reached 91%.	[139]
	Polydopamine (PDA)	— —	3.22~3.15	The photocatalytic CO ₂ reduction yield of CH ₄ by the composite was up to 1.50 μmol/g·h, which was 5 times that of pure TiO ₂ .	[140]

In summary, the modified TiO₂ photocatalyst significantly improves its photocatalytic performance in UV and visible light by increasing the specific surface area and reducing the band gap energy. The larger specific surface area increases the catalyst's active site and improves the contact efficiency with pollutant molecules, while the reduced band gap energy enables the catalyst to absorb a wider spectrum, including visible light, thereby broadening the photoresponse range and enhancing the utilization of sunlight. In addition, the specific modification method can further promote the separation and migration of photogenerated electrons and holes and further improve photocatalytic efficiency. These improvements make the modified TiO₂ photocatalyst show a broader application potential in the field of environmental governance and new energy development.

The photocatalytic performance of TiO₂ was improved to varying degrees. However, due to problems such as low efficiency, insufficient stability, and secondary pollution, TiO₂ modification methods cannot be widely used. The advantages and disadvantages of TiO₂ modification methods are shown in Table 3.

Table 3. Advantages and disadvantages of TiO₂ modification methods.

Modification Methods	Advantages	Disadvantages
TiO ₂ -doped noble metals	High specific surface area; good surface activity; good stability; characteristics of multiphase catalysis.	Inefficient use of visible light; Expensive precious metals.
TiO ₂ -doped transition metal	The presence of polyvalent transition metals promotes chemical reactions, modulates the electronic structure of TiO ₂ to improve its photocatalytic properties, and extends the light absorption range.	Prone to focusing; not environmentally friendly.
TiO ₂ -doped rare earth metals	Good stability; high catalytic activity; expanding the range of TiO ₂ light absorption and promoting photocatalytic reactions.	Complicated operating procedures; not easy to recycle.
TiO ₂ compound semiconductors	Formation of heterojunctions to expand the light absorption range of the material and improve photocatalytic efficiency. Reduction in electron-hole complex reaction.	The complexity of design and preparation.
TiO ₂ composite polymers	More environmentally friendly; Mechanical properties will be improved; Can be repeated many times.	The dispersion is not good; May degrade the polymer matrix.

5.2. Future Research Direction and Development Trend

Although TiO₂ modified photodegradation of organic pollutants has made remarkable progress, there are still some key problems and shortcomings. First, the stability of the modification effect is still a challenge, which can lead to performance fluctuations in practical applications. Secondly, the high preparation cost limits the possibility of large-scale

applications. Therefore, future research needs to further explore and optimize modification methods to improve their stability and reduce costs.

In addition, the importance of mechanism research cannot be ignored. Strengthening the mechanism study can not only provide solid theoretical support for the optimization of modification methods but also help us to understand more deeply the reaction mechanism of TiO₂ photocatalytic degradation of organic pollutants. This will lay the foundation for the design of more efficient and stable TiO₂ photocatalytic materials.

In practical applications, the effect of TiO₂ photocatalytic degradation of organic pollutants may be affected by a variety of factors, including water quality, light conditions, dye type, and concentration. Therefore, future research also needs to focus on how to optimize the performance of TiO₂ photocatalytic degradation of organic pollutants in various real-world environments.

In conclusion, optimizing the preparation method and process of TiO₂ composite photocatalytic materials has become an important direction of future research on the photodegradation of organic pollutants. By introducing visible light absorbing inorganic substances or modifying TiO₂, we can prepare multi-functional composite materials that can expand the range of light absorption and, at the same time, play the role of photocatalysis, adsorption, and catalysis, thus significantly improving the degradation efficiency of organic matter. With continuous research and exploration, we look forward to developing more efficient, stable, and environmentally friendly TiO₂ photocatalytic materials, making important contributions to environmental protection and sustainable development.

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