Impact of Titanium Dioxide (TiO$_2$) Modification on Its Application to Pollution Treatment—A Review

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Abstract: A high-efficiency method to deal with pollutants must be found because environmental problems are becoming more serious. Photocatalytic oxidation technology as the environmentally-friendly treatment method can completely oxidate organic pollutants into pollution-free small-molecule inorganic substances without causing secondary pollution. As a widely used photocatalyst, titanium dioxide (TiO$_2$) can greatly improve the degradation efficiency of pollutants, but several problems are noted in its practical application. TiO$_2$ modified by different materials has received extensive attention in the field of photocatalysis because of its excellent physical and chemical properties compared with pure TiO$_2$. In this review, we discuss the use of different materials for TiO$_2$ modification, highlighting recent developments in the synthesis and application of TiO$_2$ composites using different materials. Materials discussed in the article can be divided into nonmetallic and metallic. Mechanisms of how to improve catalytic performance of TiO$_2$ after modification are discussed, and the future development of modified TiO$_2$ is prospected.

Keywords: TiO$_2$; modification; materials; application

1. Introduction

In recent years, photocatalytic technology has attracted extensive attention because it is environmentally friendly, low-cost, and has efficient characteristics. In 1972, Fujishima et al. [1] reported that TiO$_2$ was used as a photoelectrocatalyst to split water into hydrogen. Since then, increasing research has focused on TiO$_2$. In 1976, Carey et al. [2] used photocatalytic technology to treat polychlorinated biphenyls, an organic pollution that is difficult to degrade, and experimental results found that the dechlorination rate of polychlorinated biphenyls was close to 100%. In 1977, Frank et al. [3] found that TiO$_2$ could effectively degrade cyanide (CN$^-$), which was the beginning of photocatalytic technology applied to pollution control. The degradation of photocatalytic technology can be summarized into four stages: photoexcitation, carrier capture, formation of radicals, and oxidation reaction. Compared with traditional catalytic technologies, photocatalytic technology has many advantages. First, reaction conditions such as sunlight, room temperature, and normal atmospheric pressure are common and easy to obtain. Second, the degradation processes and products of catalytic decomposition are pollution free, which are in line with the requirements of low-carbon environmental protection. Third, the characteristics of non-toxic, stable, low cost, and recyclable further promote development [4]. The core of photocatalytic technology is the photocatalyst, and many materials can act as a photocatalyst [5]. Table 1 shows the published data of different photocatalysts, including TiO$_2$ [6–8], SrTiO$_3$ [9–11], ZnO [12–14], WO$_3$ [15–17], ZrO$_2$ [18–20], and g-C$_3$N$_4$ [21–23], and their performance. Among these photocatalysts, TiO$_2$ occupies an important position due to its stable
physical and chemical properties, strong oxidation capacity, high photocatalytic activity, and excellent biocompatibility [24–26].

The TiO$_2$ can be synthesized by many methods and mainly include precipitation method, solvothermal method, sol-gel method, microemulsion method, spray pyrolysis method and electrochemical synthesis method. Zhang et al. [27] prepared the TiO$_2$/BC catalyst material by the sol-gel method and the degradation rates of reactive brilliant blue KN-R in the dyeing wastewater can reach 97%. However, there are still some problems of pure TiO$_2$ in application. The rapid recombination of photo-generated electron-hole pairs is the biggest obstacle that affect the practical application of TiO$_2$ [28], because recombination of photogenerated charge carriers can reduce the overall quantum efficiency [29]. The poor photosensitivity of TiO$_2$ under visible/solar irradiation is also a problem [30,31]. Generally, the conventional TiO$_2$ has broad intrinsic band gaps wide band gap (3.2 eV for anatase and 3.0 eV for rutile) which makes the TiO$_2$ only absorb UV radiation (wavelength < 400 nm), which accounts for only ~5% of the sunlight [32,33]. What is more, nano-TiO$_2$ is easy to agglomerate, which extremely limits the application. Therefore, in order to solve these problems and improve the catalytic activity of TiO$_2$ photocatalysts, composites have become mainstream. In addition to the improvement of photocatalysis, composites can yield other benefits. For example, composites can tune the surface properties, i.e., ability to adsorb pollutants. Composites are also beneficial toward the stabilization of nanoparticles against phenomena such as sintering or aggregation [34].

| Table 1. The published data of different photocatalysts and their performance. |
|---|
| **Type** | **Photocatalysts** | **Light Source** | **Target Pollutant** | **Degradation Rate** | **Ref.** |
| TiO$_2$ | MoS$_2$/MoO$_3$/TiO$_2$ | 300 W Xe lamp | rhodamine B | 95% | [6] |
| | Yb, Er, Ce-codoped TiO$_2$ | Xe lamp | 4-chlorophenol | 95% | [7] |
| | TiO$_2$@SiO$_2$ composites | 500 W mercury lamp | methyl orange | 99% | [8] |
| SrTiO$_3$ | La- SrTiO$_3$ | 500 W Xe lamp | Cr$^{6+}$ | 84% | [9] |
| | Ag3PO4/PANI/Cr: SrTiO3 | 300 W Xe lamp | phenol | 99% | [10] |
| | Ag, Cr-SrTiO3 | 500 W Xe lamp | methyl orange | 98% | [11] |
| ZnO | Cu-ZnO | blue light lamp | Orange II | 90% | [12] |
| | ZnO | sunlight | methylene blue | 99% | [13] |
| | Sr-ZnO | black light | methylene blue | 99% | [14] |
| WO$_3$ | WO$_3$ | 1500 W Xe lamp | N, N-diethyl-meta-toluamide | 60% | [15] |
| | WO$_3$@Cu@PDI | 300 W Xe lamp | tetracycline hydrochloride | 85% | [16] |
| | NiO-WO$_3$ | 150 W tungsten lamp | eosin yellow | 95% | [17] |
| ZrO$_2$ | Ce, Er-codoped ZrO$_2$ | halogen lamp | rhodamine B | 92% | [18] |
| | Co$_3$O$_4$-ZrO$_2$ | visible light | cyanide | 100% | [19] |
| | Cu- ZrO$_2$ | Visible light | methyl orange | 98% | [20] |
| g-C$_3$N$_4$ | Ag-P-codoped g-C$_3$N$_4$ | 8 W visible lamps | sulfamethoxazole | 99% | [21] |
| | AgI/LaFeO$_3$/g-C$_3$N$_4$ | 500 W Xe lamp | norfloxacin | 95% | [22] |
| | CdS/g-C$_3$N$_4$ | 500 W Xe lamp | rhodamine B | 96% | [23] |
The modification of TiO$_2$ to overcome the problems in the use of pure TiO$_2$ is one of the widely studied topics in the field of photocatalysis. Modified TiO$_2$ can improve its photocatalytic activity from different mechanisms, including the reduction of the band gap of TiO$_2$-based materials, the decrease of the probability of recombination between electron and hole. In recent years, different aspects are applied to improve the photocatalytic efficiency of TiO$_2$. One of the methods is ion-doped TiO$_2$ or coupled with other semiconductor composites to reduce the forbidden band width of TiO$_2$ and increase its absorption wavelength [35–37]. Another way is to deposit precious metals or metal oxides on the surface of TiO$_2$ and add electron capture agents or use photo-catalysis to prevent TiO$_2$ photo-generated electron-hole pair recombination thus improve the photocatalytic efficiency of TiO$_2$ [38–40]. In addition, dye photosensitization and providing a suitable carrier for TiO$_2$ would be the efficient methods to modify TiO$_2$ [41].

In recent years, many reviews have been conducted on the modification of TiO$_2$. Serpone [42] reviewed the different mechanisms of anion- and cation-doping TiO$_2$. He reported that TiO$_2$ photocatalysts doped with either anions or cations have recently been shown to have their absorption edge red-shifted to lower energies (longer wavelengths), thus enhancing photonic efficiencies of photoassisted surface redox reactions, and author argued that the red-shift of the absorption edge is due to the formation of color centers. Devi and Kavitha [43] reviewed the photocatalytic activity of non-metal doped TiO$_2$ for a wide variety of pollutant degradation under UV/visible light, with special emphasis on nitrogen-doped TiO$_2$. They also discussed the mechanisms of photocatalytic reactions according to the charge carrier generation–separation–transfer–recombination dynamics together with pollutant adsorption and their reactions with reactive oxygenated species in liquid or gaseous regime. Asahi et al. [44] reviewed previous studies on nonmetal-doped TiO$_2$ for visible-light sensitization. Among the enormous number of studies and references on this topic, they focused on N-doped TiO$_2$. The present review will concentrate on the application of modified TiO$_2$ in different media. First, this review summarizes the principles and types of different materials for modifying TiO$_2$. Then, it discusses the application and progress of modified TiO$_2$ in treating different pollutants. Finally, it assesses the critical application challenges and potential future research directions.

2. Non-Metallic Materials Modified TiO$_2$

2.1. Non-Metallic Materials Supported TiO$_2$

Loading TiO$_2$ on the carrier can effectively overcome the problems mentioned above [45]. At present, the non-metallic porous minerals commonly used in loading TiO$_2$ can be divided into non-metallic porous minerals, glasses, carbon materials, and polymer materials.

The treatment of polluted water by porous mineral composites has aroused attention because of the advantages of high specific surface area, strong adsorption characteristics, and the ability of targeted enrichment of pollutants with the development of non-metallic porous minerals. [46]. As shown in Figure 1, TiO$_2$ loads into the pores or surfaces of mineral materials and then forms the non-metallic porous minerals/nano-TiO$_2$ composite system, which can solve the problem of the agglomeration of nano-TiO$_2$ particles. Pollutants can be adsorbed to the surface of nano-TiO$_2$ through the ion exchange and increase the contact probability of catalysts with pollutants to improve the degradation rate. Hence, porous mineral/nano-TiO$_2$ composite systems can improve the photodegradation efficiency of nano-TiO$_2$. Liang et al. [47] used montmorillonite as the matrix to prepare a TiO$_2$/montmorillonite composite photocatalyst. The results showed that the montmorillonite matrix improved the capacity of optical absorption capacity from 70% to 87% because the visible light absorption ability (390–780 nm) of the composites was enhanced compared with pure TiO$_2$. Moreover, the ultraviolet light absorption ability of montmorillonite-supported nano-TiO$_2$ composites was improved. Therefore, adding montmorillonite carrier enhances the absorbance of visible light and ultraviolet light. Zhu et al. [48] prepared Mn-TiO$_2$/sepiolite photocatalytic material using the sol-gel method at different calcining temperatures. They found that the degradation rate of emerald dye could reach 98% when the
calcining temperature was 400 °C because sepiolite and Mn broaden the spectral response range of TiO$_2$. Saqib et al. [49] prepared a nano-TiO$_2$ supported on zeolite using the liquid impregnation method. The experimental results showed that the degradation rate of methylene blue (MB) dye by the loaded material was four times that of pure TiO$_2$ because zeolite has a UV-visible radiation transparency, which allowed the excitation of light to penetrate into opaque solid powder and reach the substrate molecules present in intraparticles spaces. Zeolite might have substantially enhanced the proximity of organic molecules to the available active sites where the degradation reaction needs to take place.

![Figure 1. The schematic diagram of non-metallic materials loading TiO$_2$.](image)

Glass has good light transmission properties and is easy to make into photoreactors with different shapes. Therefore, glass-based carriers have also received widespread attention. The form of glass carrier includes glass sheet, glass tube, glass spring, hollow glass bead, and glass fiber. Malakootian et al. [50] fixed nano-TiO$_2$ on a glass plate and the removal rate of ciprofloxacin by the composite material reached 93%. Espino-Estévez et al. [51] attached the self-made high-activity TiO$_2$ to the inner wall of the glass tube reactor by the dipping-lifting method. These results showed that the material had good photocatalytic effect and recycling performance under the ultraviolet light for the degradation of phenol, diclofenac and isoproturon. The degradation rates reached 81% for phenol, 68% for diclofenac and 57% for isoproturon. This was because the decrease of the size of the TiO$_2$ aggregates The SEM images showed that coatings prepared after milling the TiO$_2$ suspension were more homogeneous without surface aggregates, which increased the contact area with pollutants. However, the glass surface is relatively smooth, which makes TiO$_2$ have poor adhesion on it and causes uneven loading of TiO$_2$.

Combining carbon materials with TiO$_2$ can substantially improve the photocatalytic activity of TiO$_2$ mainly because C in the carbon material can effectively promote the separation of photogenerated electrons and holes as an electron trap [52]. Carbon materials include carbon fiber (CF), carbon nitride, activated carbon, carbon nanotubes, and graphene. Chu et al. [53] used the microwave hydrothermal method to load nano-TiO$_2$ on CF. The experimental results showed that TiO$_2$/CF has a good photocatalytic activity. The degradation rate of rhodamine B after 1 h of ultraviolet light irradiation reached 95%. When the catalyst was used for 10 cycles, the degradation rate of the dye still reached 88%. They also reported that compared with pure TiO$_2$ particles, TiO$_2$/CF was easily recycled when used as a photocatalyst. Nitric acid oxidation treatment of CF generated polar functional groups, which improved the bonding properties between TiO$_2$ and CF. Hu et al. [54] prepared 3D flower-like g-$C_3$N$_4$/TiO$_2$ composite spherical materials (FCTCMs) using a simple solvothermal method and studied their photocatalytic performance. The results showed that the photocatalytic performance of FCTCMs under visible light was twice that of FTM (3D flower-like structure of TiO$_2$ microspheres) because g-$C_3$N$_4$ can broaden the photoresponse range and reduce the recombination rate of photogenerated electron–hole pairs. Cunha et al. [55] prepared TiO$_2$/activated carbon composites (TiO$_2$/AC), and the
degradation rate of benzodiazapine drugs reached 98% mainly due to the sorption capacity of activated carbons. Thus, pollutants tend to be adsorbed more efficiently on the surface of the composite close to the TiO$_2$ catalyst. Moreover, TiO$_2$/AC composites enhance the generation of superoxide radicals and hydroxyl radicals.

Titanate nanomaterials (especially titanate nanotubes, TNTs) as the carriers of TiO$_2$ and the adsorbents for heavy metals have attracted great attention from researchers [56]. Because their high specific area, great ion-exchange properties, easy solid–liquid separation and abundant functional groups [57,58]. As the carriers of TiO$_2$, titanate nanomaterials can provide lots of nano-scale reactive sites when reacting with contaminants and improve the separation between catalysts and pollutants for the good sedimentation property of titanate nanomaterials [31]. Liu et al. [59] synthesized the TiO$_2$/titanate nanosheet composite material (TNS) and used of Cr(VI) and 4-cholophenol (4-CP) as the target pollutants to tested its performance. The resulted showed that the Cr(VI) removal efficiency attained 99.7% within 120 min and the removal efficiency of 4-CP was 98% within 60 min. They reported that the excellent performance was mainly because the synergetic photocatalysis and autosynchronous doping. The efficiency of the separation between electron-hole pairs was enhanced due to the combination of photo-reduction of Cr(VI) by electrons and photo-degradation of 4-CP by holes. In addition, the adsorption of the reduced Cr(III) by TNS can narrowed energy band gap and enhanced photocatalytic activity of the materials. Zhao et al. [60] constructed the TiO$_2$ decorated titanate nanotubes composite (TiO$_2$/TNTs) and used for photocatalytic degradation of bisphenol A (BPA). They compared the performance of the TiO$_2$, TNTs, and TiO$_2$/TNTs. The experiment result showed that in the first cycle, the degradation rate of BPA using TiO$_2$, TNTs, and TiO$_2$/TNTs was 100%, 5.8%, and 94% under UV light. Although the removal efficiency of BPA by TiO$_2$ is slightly higher than that of TiO$_2$/TNTs in the first cycle, reusability of TiO$_2$/TNTs was proved in the next cycles. After five reuse cycles, the degradation rate of BPA still reached 91% by using TiO$_2$/TNTs and 95.8% of the material could be separated after 6 h gravity-settling, while the 1.8% BPA was removed and 93% of TiO$_2$ will lose after gravity settling and cannot be reused in pure TiO$_2$ group. Besides, Li et al. [61], Cheng et al. [62], and Ji et al. [63] also used titanate materials modified TiO$_2$ to treated the 4-chlorophenol, phenanthrene, and sulfamethazine, respectively.

In addition, many types of polymer materials have been chosen as catalyst carriers, such as polyethylene (PE), polyvinylidene chloride (PVDF), and polyaniline (PANI) Tu et al. [64] incorporated rectorite (REC) into a porous polycaprolactone (PCL)/TiO$_2$ nanofiber and tested its photocatalytic performance. The results showed that the degradation rate of PCL/TiO$_2$/REC to rhodamine B was 98%. Because the porous PCL mats could provide large contact area for TiO$_2$. Besides, the addition of rectorite (REC) could reduce the diameters of fibers and enlarge the specific surface area, which might improve the photocatalytic efficiency. Ni et al. [65] fixed nano-TiO$_2$ nanometers in a polyvinyl alcohol–ethylene–ethylene nanofiber scaffold and tested its photocatalytic performance by using methylene blue (MB) as a target pollutant. The experimental results showed that the degradation rate of MB was 97% in 150 min. Mohsenzadeh et al. [66] synthesized the PANI-TiO$_2$ nanocomposite using the n-situ deposition oxidative polymerization method. The results showed that the material had good photocatalytic degradation performance for 1,2-dichloroethane wastewater because of the large contact area for TiO$_2$.

Although non-metallic materials loaded TiO$_2$ can improve the photocatalytic activity, there are still many problems. High-quality carriers and immobilization methods to complete the photocatalyst loading is necessary. Furthermore, the interaction between carriers and photocatalyst and its effect on catalytic efficiency need to be investigated.

2.2. Non-Metal Element Doping Modification

The doping of non-metal elements has always been a hot spot in the field of photocatalytic modification. Doping non-metal atoms can broaden the photoresponse range of TiO$_2$. Non-metal
ion doping reconstructs TiO$_2$ valence band and moves it upward, which can shorten the gap width (Figure 2).

The lifetime of photogenerated electron-hole pairs and the region of light response to visible light are vital for TiO$_2$ to increase the value in pollutant treatment [67]. In recent years, it has been found that doping non-metallic elements such as S, N, C, B, I, and F to TiO$_2$ successfully extended the optical response range of nano-TiO$_2$ to the visible light region. Non-metal element doping means that oxygen or partial oxygen in the TiO$_2$ was replaced by non-metals. The new energy band was reconstructed and the width of the forbidden band was shortened during doping the non-metal element [68–70]. As a result, the light response range was expanded. Doping non-metallic elements could increase the impurity level in the forbidden band of TiO$_2$ and help the band energy level keep higher than the reduction level, where the energy level of TiO$_2$ are overlap [71–73]. Asahi et al. [74] first replaced a small amount of lattice oxygen in TiO$_2$ with non-metallic element N doping, and successfully achieved visible light catalytic activity of TiO$_2$. The preparation method of non-metal element doped TiO$_2$ photocatalyst can be divided into post-treatment and process treatment. Process treatment means that non-metal elements was doped during the formation of TiO$_2$, and post-treatment means that non-metal elements was doped after TiO$_2$ formation.

Li et al. [75] prepared N-doped TiO$_2$ using the sol-gel method, and the degradation results of dye methylene orange (MO) showed that the degradation rate of pure TiO$_2$ was less than 5% after 180 min under visible light, whereas that using N-doped TiO$_2$ as the catalyst was over 95% after 90 min. N doping substantially enhanced the ability of TiO$_2$ to degrade MO under visible light because N impurity and Ti$^{3+}$ acted cooperatively to narrow the band gap of N-doped TiO$_2$. Jyothi et al. [76] prepared N and F co-doped TiO$_2$ using the hydrothermal method to remove bromoethane in the solution. The doping element inhibited the photogenerated electron–hole recombination to generate the hydroxyl radical (•OH). The synergistic effect increased the removal rate of bromoethane for 90 min from 54% of pure TiO$_2$ to 94%. Rahbar et al. [77] prepared S and N co-doped carbon quantum dots (CQDs)/TiO$_2$ composites using the hydrothermal method. The degradation rate of acidic AR88 (azo dyes) under visible light irradiation was 54%, which was higher than that of pure TiO$_2$. They also reported that CQDs allowed the separation of charges due to the electron transport characteristics. In addition, the surface functional group enhanced the photocatalytic activity by providing a higher adsorption capacity on the photocatalyst surface, and pollutant molecules were adsorbed on the photocatalyst surface to promote the photocatalytic reaction. Liu et al. [78] used I-doped TiO$_2$ (I-TiO$_2$)
material as the electrode of the photoreaction method. The experimental results showed that the removal efficiency of diclofenac through modified photoelectrode reached 60%, whereas only 10% was removed using the TiO$_2$ photoelectrode after 2 h (1.4 V) of visible light. Photoexcited electrons in the conduction band (CB) of TiO$_2$ can be accepted by the carbon structure due to the high electron storage capacity of carbon materials such as carbon nanotubes. Therefore, the doping of non-metal element not only extends the photocatalytic reaction to visible light, but also improves the photon efficiency of TiO$_2$ by promoting the separation of charge carriers.

Although doping non-metallic elements improves the visible light response of TiO$_2$, the band gap width reduces. As a result, the oxidizing ability of the TiO$_2$ nanocrystalline phase is directly reduced, and the adsorbed substances cannot be completely degraded. Therefore, the development of non-metal doping remains a hot and difficult issue in the field of photocatalysis.

3. Metal Materials Modified TiO$_2$

Metal materials such as stainless steel, nickel mesh and nickel foam can be used as carriers for TiO$_2$ to solve the pollutant problems. However, metals are generally expensive and damage the crystal lattice in some respects. Therefore, metals are hardly used as carriers. Since the surface of metal is similar to that of glass, it generally has poor adhesion and is difficult to load. Hence, precious metal deposition and metal ion doping are mostly used to modify TiO$_2$. At present, the metal materials which are used to modify TiO$_2$ include transition metals (Cr, Fe, and Cu) [79–81], precious metals (Ag, Au, and Pt) [82–84], and rare earth metals (Ce, La, and Nd) [85–87].

3.1. Precious Metal Materials Deposition

Precious metal materials with a large radius are easy to deposit on the surface of TiO$_2$ particles and can be used as an effective trap for electrons when a certain amount of precious metals is deposited [88–90]. As shown in Figure 3, electrons can transfer from the surface of TiO$_2$ with a higher Fermi level to the surface of the precious metal with a lower Fermi level. When the Fermi levels of the two surfaces are the same, the electrons will stop transferring and form a Schottky barrier, which can effectively separate photogenerated electron–hole pairs and improve the photocatalytic activity of TiO$_2$ [70,91,92]. Moreover, depositing an appropriate amount of precious metals on the surface of TiO$_2$ can broaden the response range of TiO$_2$ to sunlight and improve the utilization of solar energy, that is, the mechanism of depositing precious metals on the surface of TiO$_2$ to improve the photocatalytic efficiency changes the surface properties of TiO$_2$. As a result, the number of electrons on the surface of TiO$_2$ is reduced, the separation of photogenerated electron–hole pair is promoted, [93–95] and the photoelectric conversion efficiency is improved. Precious metal deposition can improve photocatalytic performance, but the deposition amount on the metal surface must be controlled within a suitable range. If the deposition amount is very large, the metal may become the center of recombination of electrons and holes, which improves the probability of the electron–hole recombination. Therefore, it is not conducive to photocatalytic degradation [96,97]. Precious metal deposition modification has a high selectivity for photocatalytic degradation of organics [98].
In the 1980s, Sato et al. [99] reported that Pt deposited on the surface of TiO$_2$ enhanced the photocatalytic efficiency of water conversion to H$_2$ and O$_2$. Later, Kennedy et al. [100] reported that the incorporation of thermally oxidizable Pt into TiO$_2$ increased the photocatalytic activity of TiO$_2$. The oxidation activity of Pt/TiO$_2$ was higher than the sum of the oxidizing properties of pure Pt and pure TiO$_2$. The improvement was due to the accumulation of holes at the Pt/TiO$_2$ interface, which led to a decrease in electron-hole recombination in TiO$_2$. What is more, the desorption of photo-oxidized intermediated on the surface of TiO$_2$ and re-adsorption on the surface of Pt with associated thermal oxidation. Ji et al. [101] prepared the Ag-Carbon-TiO$_2$ composite by using polystyrene/AgNO$_3$ composite fibers as a sacrifice template. They found that the degradation rate of Rhodamine B reached 90%, when the reaction ran 6 h. Shan et al. [102] synthesized biochar-coupled Ag and TiO$_2$ composites by mixing, calcination, and photodeposition method. They tested the photocatalytic performance of the material by using methyl orange (MO) as target pollutants. The result shows that TiO$_2$ modified with Ag showed better photocatalytic degradation performance (the highest decolorization efficiency and mineralization efficiency were 97.48% and 85.38%, respectively) than pure TiO$_2$. They attributed the increase in catalytic efficiency to the promotion of the separation of photogenerated electron hole pairs. Jaafar et al. [103] used in-situ electrochemical method to deposit Ag nanoparticles on the surface of TiO$_2$ and degraded chlorophenol to measure its photocatalytic activity. The study found that Ag-TiO$_2$ catalyst degraded chlorophenol to 94% after 6 h, for the electron–hole separation had been enhanced.

The precious metal deposition on the surface of TiO$_2$ achieves a relatively obvious modification effect that significantly increases the degradation rate of some organic compounds. However, the cost of the precious metal deposition method is very expensive and precious metal deposition modified TiO$_2$ has a high selectivity for photocatalytic degradation of organics, which further limit the application of these materials in pollution treatment.

### 3.2. Metal Ion Doping TiO$_2$

Doping different metal ions in TiO$_2$ photocatalyst is an effective method to improve its catalytic activity [80,104,105]. Metal ions doped with TiO$_2$ can change the corresponding energy level structure of TiO$_2$ because metals are more active, and electrons are more easily excited, resulting in a wider range of the absorption in a TiO$_2$ system [81,106,107]. As shown in Figure 4, metals can capture the electrons generated by TiO$_2$ excitation, and the electrons inside TiO$_2$ are not easy to return to the original state.
After metal doping, metal ions can act as a carrier-trapping center, where metal ions higher than tetravalent are more likely to acquire electrons than titanium ions and metal ions lower than tetravalent trap holes. Ion doping can then stop the recombination of electron–hole pairs, which enables TiO$_2$ to generate more electrons and holes. Thus, the photocatalytic efficiency of TiO$_2$ is improved [108,109]. For metals with many valence states, electrons in the d orbitals can transition and enter the TiO$_2$ lattice, which can reduce the band gap and the energy required for the electron transitions [110,111]. This is vital to improve the activity of TiO$_2$ photocatalyst [112]. The transition group metal ions doped with TiO$_2$ can change the crystalline morphology and energy level structure of nano-sized TiO$_2$ to form impurity energy levels [68]. Photons with lower energy can also undergo transitions, thereby expanding their absorption wavelength range and improving the utilization of visible light [113].

Figure 4. The mechanism of metal ion doping TiO$_2$.

As early as 1994, Choi et al. [114] began studying the doping of metal ions with TiO$_2$. In the experiment, 19 kinds of transition metal ions were doped into nano-TiO$_2$ and showed a better catalytic activity with the dope of Fe$^{3+}$, Mo$^{5+}$, Os$^{3+}$, and Rh$^{3+}$ due to the match of doped ionic potential and radius with TiO$_2$. Du et al. [115] used Ge$^{4+}$-doped TiO$_2$ to prepare Ge/TiO$_2$ photocatalytic materials and degraded ciprofloxacin. The radius of Ge$^{4+}$ was 0.054 nm, which was smaller than that of Ti$^{4+}$ (0.068 nm). Ge entered the TiO$_2$ lattice and replaced the position of Ti, causing lattice defects and delaying the recombination of electrons and holes. Therefore, the formation of •OH on the surface of TiO$_2$ and the photocatalytic efficiency increased. Degradation rate reached 97% when the calcination temperature was 571 °C and the doping amount was 0.26%. Crisan et al. [116] prepared Fe-doped nano-TiO$_2$ using the sol-gel method, and the absorption spectrum was extended to 546 nm. Moreover, the corresponding band width at the wavelength of 410 nm was 3.03 eV when the Fe content (w) was 2%. Compared with pure TiO$_2$, the degradation rate of nitrobenzene with 0.5% Fe nano-TiO$_2$ was increased from 70% to 88%. Gnaneskaran et al. [117] found that the spectral absorption range of Co-doped TiO$_2$ was extended from 382 to 411 nm when the band gap width was reduced to 3.01 eV. The degradation rate of MO after visible light catalytic treatment for 240 min reached 53%, which was beneficial to its photocatalytic performance. Huang et al. [118] used the sol-gel method to prepare Mo-doped nano-TiO$_2$ powders, and the degradation rate of MB reached 98% under outdoor sunlight with the amount of 2% Mo$^{6+}$ (w). This result was mainly due to the reduction of the forbidden band from 3.05 to 2.73 eV with the doping of Mo$^{6+}$ and the wider excitation absorption wavelength. Bhatia and Dhir [112] made Ni-TiO$_2$ and Bi-TiO$_2$ using the sol-gel method and found that the maximum degradation rate of ibuprofen by Bi-TiO$_2$ and Ni-TiO$_2$ reached 89% and 78%, respectively. This finding may be attributed to the increase in specific surface area and the decrease in the crystallite size. Wang et al. [119] prepared an Fe$^{3+}$-doped TiO$_2$ nanotube array catalyst using a simple hydrothermal method, which increased
the degradation rate of MB by about 20%. The study also found that Fe$^{3+}$ doping provided traps in the TiO$_2$ lattice, which greatly improved the separation effect of electron–hole pairs.

4. Composite Materials Modified TiO$_2$

4.1. The Construction the Heterojunction

The heterojunction is a contact interface, formed as a result of hybridization between two semiconductors [120,121]. The semiconductors used for the heterojunction need to satisfy the condition that they should exhibit different band gaps and the narrow band gap must lie in the visible region [122]. Combining TiO$_2$ with other semiconductors to construct heterojunction can efficiently improve the photocatalytic performance of TiO$_2$ [123,124]. This method can not only improve the effective utilization rate of the electrons by promoting the photo-generated electrons and holes to transfer in the opposite direction but also expand the spectral response range of the composite to visible light and even near infrared region [125–127]. Generally, the most widely researched types of the TiO$_2$-based heterojunction can be categorized into two different types depending on the charge carrier separation mechanism, which are conventional type and direct Z-scheme [128–130].

Based on the different band and electronic structures, the conventional type can be divided into three, namely, type-I (straddling gap), type-II (staggered gap), and type-III (broken gap) heterojunctions [131,132]. For type-I heterojunctions, the level of the CB of semiconductor-I is higher than that of semiconductor-II, while the valence band (VB) of semiconductor-I is lower than that of semiconductor-II. However, due to the difference between the band gaps, the photoinduced charges accumulate on smaller band gap semiconductor, which may cause recombination. In type-II heterojunctions (Figure 5b), the level of CB and the VB of semiconductor-II are higher than those of semiconductor-I [133]. In addition, the migration of charge carriers to the opposite directions can be promoted because the difference between the chemical potentials causes a phenomenon called band bending. The band structure of the type-III heterojunctions (Figure 5c) is similar to that of type-II except that the staggered gap becomes so wide that the bandgaps do not overlap [134]. Among these conventional heterojunctions, type-II heterojunction attracts the attention of more researchers [135–137]. Ganguly et al. [138] synthesized type-II heterojunctions of the AgBiS$_2$–TiO$_2$ composite and used doxycycline as the target pollutant to test photocatalytic performance. The results showed that the degradation rate reached 100% in 180 min under a 500 W Xe lamp. The enhanced photocatalytic activity was attributed to the decreased rate of recombination of the photogenerated excitons. Liu et al. [139] used other semiconductors such as Bi$_2$MoO$_6$ and TiO$_2$ to fabricate type-II heterojunctions and tested the photocatalytic performance of Bi$_2$MoO$_6$–TiO$_2$. They reported that the degradation rate of ciprofloxacin, tetracycline, and oxytetracycline reached 88%, 78%, and 78%, within 150 min, respectively, when the 350 W Xe lamp with a 420 nm cutoff filter was used as the light. The CB of TiO$_2$ can serve as the electron transfer platform, which can improve the efficiency of the separation of photocarriers at Bi$_2$MoO$_6$–TiO$_2$ heterojunction interface.

In 2013, the concept of the direct Z-scheme photocatalyst was first proposed [140]. Figure 5d is the band arrangement and electron migration mechanism of Z-scheme heterojunctions. The Z-scheme heterojunctions have the same band arrangement as the type-II heterojunctions, but the electron transfer path between semiconductors is different [141]. The electron transfer path between semiconductors is like the English letter “Z” [142]. In the process of photocatalytic reaction, the photogenerated electrons with lower reduction ability in semiconductor-II recombine with the photogenerated holes in semiconductor-I with lower oxidation ability. Therefore, the photogenerated electrons with high reduction ability in semiconductor-I and the photogenerated holes with high oxidation ability in semiconductor-B can be maintained [143]. In addition, the electrostatic attraction between the photogenerated electron on the CB of the semiconductor-II and the photogenerated holes on the VB of the semiconductor-I will promote the migration of the photogenerated electron from the semiconductor-II to the semiconductor-I, while in the type-II heterojunction, the electrostatic repulsion
between the photogenerated electron of the semiconductor-I and the semiconductor-II will inhibit the transfer of electrons from semiconductor-I to the semiconductor-II [144,145]. So far, many photocatalytic composites that have the Z-scheme heterojunctions have been manufactured to degrade the pollutants. Wang et al. [146] fabricated the N-doped carbon quantum dot (NCDs)/TiO$_2$ nanosheet with higher surface energy faceted (NCDs/TNS-001) composites and used diclofenac (DCF) as the target pollutants. The photocatalytic efficiency of the composites reached 92% in 60 min under the 350 W Xe lamp. In contrast, only 15.4% of the DCF was degraded in the presence of TNS-001 after 60 min. They reported that the excellent photocatalytic performance might be attributed to the synergistic effects of the highly active facets, up-converted fluorescent properties of NCDs, and efficient charge separation induced by fabricated Z-scheme heterostructures. Hao et al. [147] used the TiO$_2@g$-C$_3$N$_4$ core-shell photocatalysts with the Z-scheme heterojunctions to remove the Rhodamine B from water. The removal efficiency under the 100 Xe lamp was about 96% within 180 min, while the Rhodamine B (RhB) dye shows almost no degradation in the blank test. They attributed the improvement of photocatalytic performance to the formation of the Z-scheme system, which effectively separated photogenerated electrons and holes. Liao et al. [148] prepared a photocatalytic material g-C$_3$N$_4$–Ti$_3^+/TiO_2$ nanotube arrays and tested its performance of degrading the phenol. At a reaction period of 7 h, the degradation was only 23.4% using TiO$_2$ nanotube arrays, while the degradation rate increased to 74% using the g-C$_3$N$_4$–Ti$_3^+/TiO_2$ nanotube arrays. This was mainly because that the self-doping of Ti$_3^{3+}$ promoted the visible light absorption behavior of the composite and the Z-scheme heterojunctions with efficient space separation of the photo-generated electron–hole.

![Figure 5.](image)

**Figure 5.** The band arrangement and electron migration mechanism of different heterojunctions. (a) Type-I heterojunction; (b) Type-II heterojunction; (c) Type-III heterojunction; (d) Z-scheme heterojunction.

Semiconductor heterojunction powders have exhibited the enhanced photocatalytic activities, but their practical applications have been limited due to their poor recycling performance from flowing wastewater.
4.2. Different Elements Co-Doping TiO$_2$

The emphasis of single element doping on the modification of TiO$_2$ is different. In order to improve the migration range of absorption edge, photocatalytic performance and thermal stability of TiO$_2$ at the same time, the co-doping of multiple elements is an ideal solution [149]. Co-doped nanoparticles exhibit higher visible light absorption than single doped TiO$_2$ due to a synergistic effect between the two dopants, which can efficiently increase the photocatalytic performance [150]. Co-doping can be divided into different metal elements co-doping [151–153], metal elements and non-metal elements doping [154–156] and different non-metal elements doping [157–159]. As shown in Table 2, many researchers have used co-doping method to modify TiO$_2$ and tested the photocatalytic performance of the materials.

| Doping Elements | Crystal Phases of TiO$_2$ | Light Source and Reaction Time | Target Pollutant | Degradation Rate | Ref. |
|-----------------|---------------------------|--------------------------------|-----------------|-----------------|-----|
| Ni, Cr          | anatase                   | Sunlight 90 min                | methylene blue  | 96%             | [153]|
| Cu, Co          | anatase                   | LED 300 min                    | acetaldehyde    | 99%             | [160]|
| Ag, V           | -                         | 40 W white light bulbs 180 min | hexane gas butyl acetate gas | 94% 96% | [161]|
| N, Cu           | anatase                   | 200 W Xe lamp 60 min           | sulfamethoxazole | 99%             | [162]|
| Fe, I           | anatase                   | visible light 60 min           | gaseous benzene | 59%             | [80] |
| Mn, N           | anatase, rutile, wurtzite | LED 40 min                     | Quinalphos 2-chlorophenol | 92% 88% | [163]|
| N, Ag           | anatase                   | LED 360 min                    | methylene blue  | 99%             | [164]|
| Ag, Pd, N       | anatase                   | mercury vapor lamp 120 min     | malachite green methylene blue | 75% 92% 62% | [165]|
| C, N            | anatase                   | simulated sunlight 420 min     | 4-nitrophenol   | 87%             | [166]|
| N, F            | anatase                   | 500 W Xe lamp 150 min          | methylene blue  | 89%             | [167]|
| Si, N           | anatase                   | 500 W Xe lamp 180 min          | Rhodamine B     | 86%             | [168]|
| C, N            | anatase and rutile        | 300 W Xe lamp 150 min          | phenol          | 92%             | [169]|

At present, the physical and chemical properties and the doping mechanism of co-doped TiO$_2$ with two different metals have not been thoroughly investigated. Singh et al. [170] synthesized the mesoporous La-Na co-doped TiO$_2$ nanoparticles (NPs). The removal efficiency of MB was almost 100% by using the Na and La doped TiO$_2$, while 35% MB was degraded by using pure TiO$_2$ mainly because of the substitution of large-sized Na$^{+}$ and La$^{3+}$ at Ti$^{4+}$ sites which was confirmed by the results of XRD and TEM. The doping of these low-valent metal ions led to the formation of O vacancies, which promoted the adsorption of hydroxyl groups on the surface of NPs. The adsorbed hydroxyl group reduced the pH$_{IEP}$, which was beneficial to the adsorption of cationic MB dyes. Metal components prefer to substitute for the Ti site in the TiO$_2$ lattice to create the dopant level near the CB. Non-metal components can form new levels closest to the VB that reduce the band gap and cause visible light absorption. Therefore, metal and non-metal ion co-doping enhance photocatalytic activity [163,171]. Garg et al. [172] tested the photocatalytic performance of prepared N and Co-co-doped TiO$_2$ on the removal of Bisphenol-A under visible light. The results showed that the maximum degradation rate
(95%) was observed when using 1.5% Co and 0.5% N co-doping TiO$_2$. This result was almost twice that of the group using pure TiO$_2$. TiO$_2$ was enhanced because Co and N disturbed the physical properties of the nano particles, producing alterations in crystal structure and energy band gap as well as elemental composition. N could easily substitute O in the TiO$_2$ lattice owing to its atomic size comparable with that of O, and N had small ionization energy and high stability. In addition, the doping of a range of Co could shift the optical absorption edge from UV to visible light range, and Co could behave as recombination centers for the photoinduced charge carriers, thereby decreasing quantum efficiency. Non-metal co-doped TiO$_2$ have been studied extensively [173–175]. Zeng et al. [176] prepared B/N co-doped TiO$_2$ photocatalysts and compared their photocatalytic performance with pure TiO$_2$ under simulated sunlight by using flumequine (FLU) as the target compound. The results showed that the degradation rate of FLU by B/N co-doped TiO$_2$ was nearly 100%, whereas that of pure TiO$_2$ was only about 10%. The photocatalytic performance of TiO$_2$ catalyst was evidently enhanced by B/N co-doping. The relative content of rutile in B/N co-doped TiO$_2$ catalysts increased with the increase of the B content, which produced a synergistic effect between anatase and rutile. This synergistic effect can be explained by the formation of a semiconductor junction between the anatase phase and the rutile phase, which promoted the separation of photogenerated electrons and holes, thus improving photocatalytic activity.

The method of co-doping can effectively improve the removal efficiency of pollutants by TiO$_2$. But some of the elements are not suitable for practical use, so it is necessary to find suitable doping materials. And it is essential to find an optimum amount of dopant to increase the separation of charge carriers and prevent the formation of a recombination center.

4.3. Dye Photosensitization

Dye photosensitization means that the photosensitizer (dyes) binds to TiO$_2$ surface by chemical or physical adsorption, so that the absorption wavelength of visible light shifts to the long wavelength, thus expanding the excitation wavelength response range of TiO$_2$ and greatly improving the utilization of sunlight [177–179]. The molecule (dyes) absorbing the photon is called as a photosensitizer and the altered material (TiO$_2$) is the acceptor or substrate [180]. As shown in Figure 6, the mechanism of photosensitization is that once the dyes achieve their excited state by the absorption of photons in the visible range of the solar spectrum, electrons from the dyes’ highest occupied molecular orbital (HOMO) are transferred to their lowest unoccupied molecular orbital (LUMO) and subsequently to the conduction band (CB) of TiO$_2$ [181–183]. In addition, the dyes in solution can be excited to a triplet state under visible light and transfer their excess energy to the O$_2$. Thus, the electrons in the LUMO react with dissolved oxygen and produce the superoxide anion radical [184]. Dyes used for photosensitization must meet the following characteristics: strong absorption of visible light even the part of the near infrared (NIR) region, photo stability (unless the self-sensitized degradation is required), the existence of some anchoring groups (-SO$_3$H, -COOH, -H$_2$PO$_3$, etc.) and the higher excited state energy than the conduction band (CB) edge of TiO$_2$ [185,186]. According to the composition, dyes can be divided into two categories: organometallic dyes and organic dyes. Organometallic dyes contain a transition metal in the structure and the organic dyes are composed of organic chromophores [187].
Further research is needed to solve these problems.

The modification method of photosensitization can greatly improve the photocatalytic performance of titanium dioxide. However, there are still some problems need to be solved. For example, the organic dye molecule will gradually degrade due to the photocatalytic. So, it is necessary to replace the catalyst continuously. Additionally, the absorption of most photosensitizers is weak in the near-infrared region and there is adsorption competition with pollutants, which limits the development of photosensitization. Therefore, further research is needed to solve these problems.

5. **Application of Modified TiO₂ Composite Photocatalytic Materials**

Photocatalytic treatment technology is the most representative advanced oxidation technology for environmental pollution treatment. It uses the hydroxyl radical (•OH) as a strong oxidant to deeply oxidize and decompose organic pollutants into non-toxic inorganic small molecules [191]. At the same time, the photocatalytic reduction reaction can effectively remove heavy metal ions. Table 3 is the performance of the modified TiO₂ in treating pollutants.
Table 3. The performance of the modified TiO\(_2\) in treating pollutants.

| Photocatalysts | Crystal Phases of TiO\(_2\) | Light Source and Reaction Time | Target Pollutant | Degradation Rate | Ref. |
|----------------|-----------------------------|-------------------------------|------------------|------------------|------|
| TiO\(_2\)-biochar | anatase | 500 W mercury lamp 150 min | methyl orange | 97% | [192] |
| Fe\(^{3+}\)-TiO\(_2\) nanoparticles | anatase | 150 W Xe lamp 240 min | 4-chlorophenol ethyl orange | 65% 95% | [193] |
| TiO\(_2\)-Fe-porphyrin-conjugated microporous polymers | anatase | Xe lamp 90 min | methyl orange | 96% | [194] |
| Gd-TiO\(_2\) polypyrrrole@TiO\(_2\) | anatase | visible light 93 min | methylene blue | 28% | [195] |
| W, F-TiO\(_2\) sodium borosilicate glass | anatase | Sunlight 300 min | indigo carmine dye | 92% | [198] |
| TiO\(_2\)-ZrTiO\(_4\)-SiO\(_2\) | anatase | 300 W Xe lamp 90 min | rhodamine B | 95% | [199] |
| TiO\(_2\)-W\(_{18}\)O\(_{49}\) | anatase | visible light 60 min | rhodamine B | 82% | [200] |
| C/Fe-TiO\(_2\) coated on activated carbon terephthalic acid functionalized | anatase | 36 W compact light 140 min | rhoda mine B | 99% | [201] |
| g-C\(_3\)N\(_4\)/TiO\(_2\)/Fe\(_3\)O\(_4\)/SiO\(_2\) | anatase | 8 W compact fluorescent lamps 120 min | ibuprofen | 97% | [202] |
| Cu-TiO\(_2\) | anatase | 500 W Xe lamp 140 min | formaldehyde | 100% | [203] |
| MIL-101(Fe)/TiO\(_2\) | anatase | Sunlight 30 min | tetracycline | 93% | [204] |
| WO\(_3\)/TiO\(_2\) | anatase | 500 W Xe lamp 60 min | paracetamol | 100% | [205] |
| MoS\(_2\)/TiO\(_2\)/Carbon Fiber | rutile | visible light 60 min | tetracycline | 93% | [206] |
| Bi2S3/TiO\(_2\)/Montmorillonite | anatase | mercury vapor lamp 120 min | ketoprofen | 90% | [207] |
| TiO\(_2\)-reduced graphene oxide (TiO\(_2\)-rGO) | anatase | simulated sunlight | formalin | 98% | [208] |
| TiO\(_2\)/glass | anatase | Sunlight 30 min | 2,5-dichlorophenol | 95% | [209] |
| Bi, B-TiO\(_2\) | anatase | Xe lamp 90 min | 5-fluorouracil | 100% | [210] |
| Ce, Mn- TiO\(_2\) | anatase | 30 W ultraviolet lamp 240 min | diclofenac | 94% | [211] |
| Fe-TiO\(_2\) | anatase | visible light 1050 min | acetaldehyde | 65% | [212] |
| N, F-TiO\(_2\) | anatase | mercury vapor lamp 180 min | ethylbenzene | 33% | [213] |
| activated carbon-TiO\(_2\) | anatase | UV light 20 min | toluene | 99% | [214] |
| Eosin Y- TiO\(_2\) | anatase | visible light 180 min | acetaminophen diclofenac | 71% 83% | [185] |
| Cu-TiO\(_2\) combine with activated carbon fiber | anatase | fluorescent lamp 180 min | Benzene toluene | 81% 98% | [215] |

5.1. The Application in Water Pollution

Wastewater treatment plants can remove a large majority of the pollution. However, several trace organic compounds or refractory compounds cannot be degraded by the conventional treatment [216]. These pollutants mostly result from domestic and industrial use of pharmaceutical preparations, printing and hygiene products, and pesticides. In recent years, photocatalytic technology has broadened its application in the treatment of organic wastewater. Under the conditions of sufficient O and light, TiO\(_2\) uses the photogenerated electrons and holes to degrade almost all organic pollutants in water and convert them into CO\(_2\), H\(_2\)O, and other inorganic substances. Saif et al. [217] prepared lanthanide (Nd\(^{3+}\), Sm\(^{3+}\), Eu\(^{3+}\), Gd\(^{3+}\), Dy\(^{3+}\), and Er\(^{3+}\))-doped TiO\(_2\) using the sol-gel method and evaluated their photocatalytic activity in the treatment of actual sewage. In the actual sewage treatment plant application, the mineralization efficiency of Gd\(^{3+}\)-TiO\(_2\) and Eu\(^{3+}\) TiO\(_2\) on chemical oxygen
demand (COD) reached 67% and 50%, respectively, after 6 h of light. Lima et al. [218] used Ag/TiO₂ photocatalytic material to degrade the hormones which would exist in the sewage treatment plant. The results showed that the degradation rate of the hormone by Ag/TiO₂ reached 95% after 3.5 h. In addition to organic pollutants, photocatalytic technology can achieve better treatment of inorganic substances in water. Peng et al. [219] prepared TiO₂-CuO/HSC composites. Degradation rates of ammonia nitrogen in water reached 61% and 100% when experiments were operated under ordinary light and ultraviolet light, respectively.

Dyeing wastewater discharged from printing and dyeing factories contains a large number of dye molecules. These dye molecules usually contain a mine groups, aromatic rings, azo groups, etc. Therefore, the chromaticity of dye wastewater is difficult to meet standards for discharge. Traditional biological and physical treatment methods for removing organic pollutants, which include precipitation, adsorption, flocculation, reverse osmosis, and ultrafiltration, are inefficient and unsuitable for industrial applications. So, people choose photocatalytic degradation as an alternative technology to solve the pollutants [220–222]. TiO₂ can not only effectively remove the color of wastewater, but also decomposes the pollutants into small molecules such as CO₂ and H₂O. Xu et al. [223] successfully prepared Ag/TiO₂ layered structure and reported the degradation rate of the dye under the sunlight reached 99%, while the degradation rate of pure TiO₂ was 43%. Ji et al. [224] used C/TiO₂ microsphere to degrade the rhoda mine B. The results showed the degradation rate of rhoda mine B reached 96% within 140 min, and the degradation rate still maintained above 80% after the material was used for three times. Fu et al. [225] use graphene oxide/TiO₂ (GO/TiO₂) composites to degrade the dyes and reported the degradation rate of the dyes reached 96% within 2.5 h.

Tannery wastewater is also a major problem in industrial wastewater because of the containing of large amounts of poorly biodegradable organic chemicals. The general biological treatment method can make the effluent reach the standard, but it still needs multiple treatments to remove most of the COD, color and some organic recalcitrant compounds. So, the photocatalytic treatment using TiO₂ become a new method to treat tannery wastewater. He et al. [226] used Mn-doped TiO₂ material to degrade the tannery wastewater. The degradation rate of organic pollutants under sunlight was nearly 90%. Bordes et al. [227] deposited the fine-structured photocatalytic TiO₂ coatings on austenitic stainless steel coupons by atmospheric plasma spraying (APS) and the total organic carbon (TOC) removal reached 49%, while the decolorization rate reached 75%. Therefore, they reported that the decreased TOC and color removal of the resulting effluent evidenced the effectiveness of the developed coatings for photocatalytic treatment of industrial tannery wastewater.

The large-scale use of pesticides such as herbicides and insecticides have a significant impact on aquatic environment. The harmful effects of these compounds are due to their toxicity and high mobility and persistence in aqueous media [228]. In fact, only a small part of the applied pesticides can protect agricultural products, while most pesticides are lost to the environment through volatilization, hydrolysis, photolysis, or degradation by microbial action [229]. The characteristics of pesticide wastewater lead to ineffective treatment by physical and biological methods, so photocatalytic oxidation is used to treat this type of wastewater, for example organophosphorus pesticides can be mineralized and decomposed by TiO₂ and converted into non-toxic CO₂, H₂O, and PO₄³⁻. Abdennouri et al. [230] prepared a nano-TiO₂ supported on pillared clay and found that the material can efficiently degrade 2,4-dichlorophenoxyacetic acid, 2,4-dichlorophenoxypropionic acid, and other pesticides in the environment. Both of the degradation reached about 80%.

As an important component of energy, petroleum plays a decisive role in the sustained and rapid development of the national economy. Due to river convergence and marine accidents, a large amount of low-density and water-insoluble oil flows into the ocean every year, causing marine oil pollution and threatening to marine life. Traditional processing is performed by mechanical methods, and biological processes are often used as auxiliary processing steps, followed by advanced processes such as adsorption, membrane filtration, and reverse osmosis. However, due to the presence of high concentrations of toxic aromatic and aliphatic hydrocarbons in addition to the presence of phenols and
refractory compounds, the biological processes cannot meet the standard of reuse [231,232]. Studies have shown that TiO$_2$ photocatalysts can float on the water surface and are efficient in the degradation of toxic and recalcitrant pollutants [233]. Shivaraju et al. [234] prepared N-doped TiO$_2$. They reported the degradation rate of oil and grease and other organic pollutants in wastewater can reach about 90%.

The pollution of pharmaceuticals in industrial wastewater is a serious problem. Traditional wastewater treatment removes most of the pollutants through sedimentation, filtration, adsorption, or biological processes, however, bio-toxic and non-degradable organics usually remain in the water at concentrations above the ppb discharge or reuse limit [235]. Using TiO$_2$ for photocatalytic reaction would be a good method to solve this problem. Solís-Casados et al. [236] used Sn-doped TiO$_2$ to treat diclofenac, paracetamol, and ibuprofen under visible light. The results showed the maximum removal rate of diclofenac was 25%, the maximum removal rate of paracetamol was 25%, and the removal rate of ibuprofen was 18%. All of the three drugs were effectively reduced. Malakootian et al. [237] used Fe$^{3+}$ doped TiO$_2$ materials to degrade pharmaceutical wastewater and antibiotic-added synthetic solutions. The results showed that the degradation rates of antibiotics can reach 70% and 97%, respectively. Besides, Lcerda et al. [238] and Hou et al. [239] also used the TiO$_2$ to degrade the pharmaceutical wastewater and obtained satisfactory results.

5.2. The Application in Air Pollution

Cars provide convenience for people’s travel, but the automobile exhaust gas seriously affects air quality and endangers people’s health. NO$_x$ in automobile exhaust not only stimulates the human respiratory system, but also causes problems such as acid rain and photochemical smog. So, the removal of NO$_x$ has attracted people’s attention. However, the traditional technologies of NO$_x$ removal, including physical adsorption and selective catalytic reduction, cannot remove the NO$_x$ effectively at ppb levels [240,241]. TiO$_2$ photocatalyst provides an effective way to solve these problems by mixing in paint, concrete and brick or fixing on the surface of roads and walls. Under sunlight, the TiO$_2$ photocatalyst can oxidize NO$_x$ to form nitric acid through a series of reactions. Then the nitric acid reacts with the components fixed the photocatalyst to obtain nitrate. Under the action of rainwater, nitrate ions are formed and washed away. Zhang et al. [242] found that nano-TiO$_2$/diatomite composites efficiently degraded formaldehyde in the air, showing a good application prospect. Qin et al. [243] found that loading nano-TiO$_2$ in concrete during road construction could absorb NO$_2$ in locomotive exhaust, thereby reducing air pollution.

Besides, most volatile organic compounds (VOCs) in air (aldehydes, ketones and alcohols) are oxidizable, it is feasible to remove them by oxidation method. Most of the heterogeneous catalytic oxidation methods commonly used to remove pollutants in the air at high temperatures, which limits the application. Therefore, the photocatalysis method has become a potential method to remove air pollutants by using water vapor and O$_2$ in air at room temperature with low energy consumption [244,245]. Lai et al. [246] prepared Bi-TiO$_2$ to degraded toluene and the degradation rate increased by 77% in terms of CO$_2$ production, as compared to the pure TiO$_2$. Rao et al. [247] used Er$^{3+}$ doped TiO$_2$ and reported the modified TiO$_2$ exhibited higher photoactivity in comparison with the pure TiO$_2$. The highest removal efficiency of acetaldehyde and o-xylene within 100 min was 99% and 85%, respectively, and ethylene degradation efficiency reached 22% within 180 min.

5.3. The Application in Soil Pollution

There are many types of soil pollutants, which are characterized by the coexistence of emerging and old pollutants. These pollutants include heavy metals, pesticides, antibiotics, and persistent organic compounds, which makes it difficult to get an efficient repair result in soil. Heavy metal pollution and organic pollution are regarded as the main types of soil pollution because of the large amount among the pollutants [248]. The surface of the contaminated soil with a high concentration of pollutants can easily enter the atmosphere or water under the action of wind and water, respectively, leading
to other secondary environmental problems such as air pollution, surface water and groundwater pollution [249–251]. Therefore, soil remediation is imminent.

The pollutants’ treatments in soil mainly include physical–chemical remediation technology, biological remediation technology, and phytoremediation technology, but all of these have some shortcomings. The photocatalytic technology can completely mineralize the organic pollutants and remove the heavy metals in the soil. This technology also has the advantages of fast decomposition rate, no secondary pollution, and easy operation [252–254]. In recent years, photocatalysis has been widely used in organic soil remediation studies, including organic pesticides, aromatic organics, petroleum hydrocarbons, and heavy metals [255,256].

TiO$_2$ is the most widely used catalyst in photocatalyst technology, and it also acts as a key role on pollutants in soil. Kuang et al. [257] reported that the Cd(II) removal efficiency of biological soil crusts increased by 27% than that of pure biological soil crusts after the addition of nano-TiO$_2$. They reported that in the first 30 min, the adsorption rate of BSC + TiO$_2$ composite was faster than that of pure TiO$_2$, which may be due to the high adsorption rate of nano-TiO$_2$. Petroleum-contaminated soil is highly toxic, and photocatalytic degradation using TiO$_2$ can also get the ideal results. Yang et al. [258] pretreated the soil with ultraviolet radiation C (UVC) activated TiO$_2$ under varying moisture conditions to enhance biodegradation of heavy hydrocarbons (HCCs). They reported that total petroleum hydrocarbon (TPH) removal after 24 h exposure to UVC was about 20% in slurries with 300% water holding capacity. In a 10 d bioremediation test, TPH removal in treated soil increased to 27%, compared to 15% for controls without photocatalytic pre-treatment. The improvement mainly because the recalcitrant hydrocarbons were transformed into more bioavailable and biodegradable products so that the pollutants were more readily consumed by soil microorganisms.

Soil remediation of modified TiO$_2$ has achieved some effects in heavy metal pollution and organic pollution, but there are still some problems, including the insufficient light penetration and difficulty in recycling. Therefore, it is necessary to find TiO$_2$ composite materials that can make fuller use of sunlight in the soil or improve the recycling rate.

6. Conclusions and Perspective

Despite the substantial progress in TiO$_2$, considerable opportunities and challenges remain. The synthesis and improvement of TiO$_2$ has become a hot topic to improve the efficiency of environmental treatment. This review comprehensively discusses several synthesis and doping technologies of TiO$_2$, and the effect of each improvement method. Moreover, it elaborates and prospects the application of TiO$_2$-modified materials in the environmental field, especially for water, air, and soil pollution.

Developing a pollutant treatment with visible light-responsive photocatalysts is very urgent and necessary. The photocatalytic performance of TiO$_2$ can be greatly improved through the modification of TiO$_2$. However, many problems in application remain to be solved: (i) in many studies, the system has only one kind of pollutant, which does not match the complex multiple components of the actual pollutants. Gaps exist between material research and application studies for practical application. Whether modified TiO$_2$ can perform well is unknown. Although modified TiO$_2$ shows potential in the treatment of pollutants, most of the works considered in the scope of this review were carried out on a laboratory scale. (ii) The recycling or natural degradation of the modified materials remains an issue. Few studies were devoted to separation, recovery, and reuse of photocatalytic materials for the treatment of the real pollutants. (iii) Introduction of other materials into TiO$_2$ will cause the preparation complexity and cost to increase. Materials used for modification may pollute the environment, such as in modification with heavy metal ions or harmful organic.

Future research should focus on the following aspects to improve the applicability and feasibility of the modified TiO$_2$: (i) more pilot experiments using modified TiO$_2$ should be performed for photocatalytic degradation of real pollutants in water, air, and soil. An understanding of inherent charge transfer dynamics and photocatalytic mechanisms at the nanometer and atomic level will be highly useful in designing effective approaches for enhancing the photocatalytic performance of
TiO$_2$. Thus, researchers should understand the mechanism of dealing with actual pollutants. (ii) The efficiency and photostability of the modified TiO$_2$ must be improved. The performance of modified TiO$_2$ is currently limited by the physicochemical properties of these materials. (iii) Materials used to modify TiO$_2$ that cause low harm to the environment and can be used in large patterns must be found or synthesized. Devising an appropriate photocatalyst immobilization strategy to provide a cost-effective solid–liquid separation can save cost and avoid secondary pollution. (iv) A good reactor can improve the utilization rate of light and reduce the electricity costs. Thus, a good design of the reactor is necessary before the experiment. (v) In several cases, toxicity assessment may be even more sensitive than chemical analysis by using modified TiO$_2$. (vi) Although modified TiO$_2$ can have a good degradation effect on pollutants in the laboratory, the durability and recyclability of the catalysts must be considered in actual application.

Facing the problems of complex types of pollutants and tight treatment time, the comprehensive application of multiple treatments for pollutants is the development direction of the current environmental field. The combined use of photocatalysis and other technologies will broaden the application of photocatalysis technology.

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