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Preparation and Photocatalytic and Antibacterial Activities of Micro/Nanostructured TiO_2-Based Photocatalysts for Application in Orthopedic Implants

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Micro/nanostructured TiO_2, ion-doped TiO_2, and heterojunction TiO_2 composite photocatalysts have low toxicity, high biocompatibility, and high photocatalytic and antibacterial activities and have broad applications in the fields of photocatalytic, antibacterial, and orthopedic implants. The photocatalytic and antibacterial activities of TiO_2 and TiO_2-based photocatalysts depend on their preparation methods. In this review, the preparation methods of TiO_2, ion-doped TiO_2, and heterojunction TiO_2 composite photocatalysts and their effects on photocatalytic and antibacterial activities were reviewed. Based on the excellent physical and chemical properties of TiO_2, ion-doped TiO_2, and heterojunction TiO_2-based photocatalysts, their applications in the field of orthopedic implants were reviewed. Meanwhile, the development trend of the photocatalyst in the fields of photocatalysis, bacteriostasis, and medicine was prospected. The purpose of this review was to point out the direction for further study on photocatalytic and antibacterial activities and related applications of TiO_2 and TiO_2-based photocatalysts.

Keywords: TiO_2, heterojunction, photocatalytic activity, antibacterial activity, orthopedic implants

1 INTRODUCTION

The development of global economy has brought comfortable material living conditions and various conveniences to the people of the world, but at the same time, it has caused great pressure on the environment (Tiwari et al., 2022). Dyes are closely related to the clothes people wear, the paper they use, and the packaging of food and medicine. The use of these dyes discharges a large amount of organic dye wastewater into rivers, resulting in water pollution (Chow et al., 2021; Feng et al., 2021; Liu et al., 2022a). The most effective method to kill the pollution of organic dye is at the source, to solve the pollution of organic dye wastewater. Therefore, the development of new technical means to degrade organic dyes has become an urgent task to solve water pollution and has received extensive attention from all over the world.

In order to solve the problem of environmental pollution, the world's developed countries associated together at all costs to solve this problem. Through unremitting efforts, many effective means have been developed to solve the problem of water pollution (Wang et al., 2019; Wang et al., 2020a; Wang et al., 2020b; Shifa Wang et al., 2020; He et al., 2021a; Wang et al., 2021a; Cheng et al., 2021; Mateo et al., 2021; Saheed et al., 2021; Han et al., 2022; He et al., 2022), including 1) the thermal catalysis technique driven by thermal energy; 2) the electrocatalytic technology driven by electricity; 3) the photocatalysis technique driven by light energy; 4) the ultrasonic catalytic technology driven by mechanical energy; 5) the biodegradation technology, which uses microbial degradation; 6) adsorption techniques, using physical or chemical properties or diffusion; and 7) the new catalytic technology using heat, light, electricity, and other methods. Among these catalytic technologies, the photocatalytic technology is a green catalytic technology that uses sunlight to achieve degradation of organic dyes. In order to realize the effective degradation of organic dyes, the selection of a suitable photocatalyst is very important.

Among many photocatalysts, TiO_2 photocatalysts have the longest research history (Fujishima and Rao, 1997). TiO_2 has three phases: tetragonal, orthogonal, and monoclinic phases. It has an optical band gap of 3.2 eV, can respond to ultraviolet light, and is a good ultraviolet photocatalyst, which has a wide range of applications in the industrial degradation of organic dyes (Wu and Yu, 2004). Meanwhile, it has high antibacterial activity and also has a wide range of applications in the fields of photocatalytic and antibacterial implants (Skorb et al., 2008). However, due to its large optical band gap value, it is difficult to respond to visible light, and the visible light occupies the majority of sunlight, which limits its application in the field of photocatalysis or photocatalytic and antibacterial implants (Dalton et al., 2002). Therefore, researchers have adopted many methods to improve the photocatalytic and antibacterial activities of TiO_2. 1) TiO_2 photocatalysts with a special defect structure were synthesized under extreme conditions. TiO_2 photocatalysts synthesized under such extreme conditions have a high specific surface area, which introduces a large number of defects and makes it have a high surface active site, thus enhancing its photocatalytic and antibacterial activities (Qu and Kroes, 2007; Li et al., 2017; Li et al., 2021a). 2) An atom with a similar radius to the Ti atom is selected for doping, and the optical band gap value of TiO_2 is reduced to achieve the purpose of responding to visible light. This method allows the atom to be doped to occupy the position of the Ti atom, but not many atoms can be doped. If the synthesis method is not chosen correctly, it can easily form composites (Colón et al., 2006; Cong et al., 2007; Zaleska, 2008). 3) Special preparation technology to construct a special heterojunction structure or surface-modified TiO_2 photocatalysts to enhance the photocatalytic or antibacterial activity of TiO_2 photocatalysts was developed (Chen et al., 2010; Bai et al., 2015; Martins et al., 2016). This method does not change the optical band gap value of TiO_2, and it combines one or more excellent physical and chemical properties of semiconductors so that the new TiO_2-based photocatalyst combined together has enhanced or novel physical and chemical properties.

In this study, the preparation methods of TiO_2, ion-doped TiO_2, and TiO_2-based composite photocatalysts are reviewed, and the effects of preparation methods on the physicochemical properties of TiO_2-based photocatalysts are summarized. Meanwhile, the photocatalytic and bacteriostatic activities of TiO_2, ion-doped TiO_2, and TiO_2-based composite photocatalysts in degradation of organic pollutants and antibacterials were reviewed. Based on the review of photocatalytic and antibacterial activities of TiO_2-based photocatalysts, the photocatalytic and antibacterial mechanisms and application of TiO_2-based photocatalysts in orthopedic implants were summarized. This review puts forward the future development direction of TiO_2-based photocatalysts and provides corresponding technical reference for expanding the study of other photocatalysts.

2 PREPARATION OF MICRO/NANOSTRUCTURED TiO_2-BASED PHOTOCATALYSTS

The photocatalytic and bacteriostatic activities of the micro/nanostructured TiO_2-based photocatalyst strongly depend on the preparation method (Nakata and Fujishima, 2012; Daghrir et al., 2013; Guo et al., 2019). TiO_2-based photocatalysts synthesized by using different preparation methods may have the advantages of large specific surface area, large surface defect concentration, and high charge carrier transfer and separation efficiency, thus greatly improving the photocatalytic and antibacterial activities of the system (Zhang et al., 1998; Choi et al., 2010).

2.1 Preparation of Micro/Nanostructured TiO_2 Photocatalysts

With the rapid development of technology, the preparation method of TiO_2 has also been in rapid development. But, really summed up, there are only two methods: physical and chemical methods. Physical methods mainly include the solid phase sintering method, vacuum evaporation, vapor phase transfer deposition, and sputtering method. Pure TiO_2 prepared by using the physical method is mainly in the form of a film, and as a photocatalyst, it has the disadvantages of having a small contact area and low photocatalytic efficiency. Chemical methods mainly include the gas-phase and liquid-phase preparation method. The commonly used gas-phase methods for the preparation of TiO_2 include gas fuel combustion, gas phase oxidation, and the atmospheric microwave plasma gas-phase method. The liquid phase methods include the sol–gel method, inorganic salt hydrolysis method, solvothermal method, micro-emulsion method, hydrolysis, hydrothermal method, HCl–water volatilization-assisted precipitation method, and polyacrylamide gel method (Macwan et al., 2011; Yu et al., 2009; Fan et al., 2009). Ren et al. (2022) prepared the TiO_2 nanoparticles by using the HCl–water volatilization-assisted precipitation method, which exhibit high photocatalytic

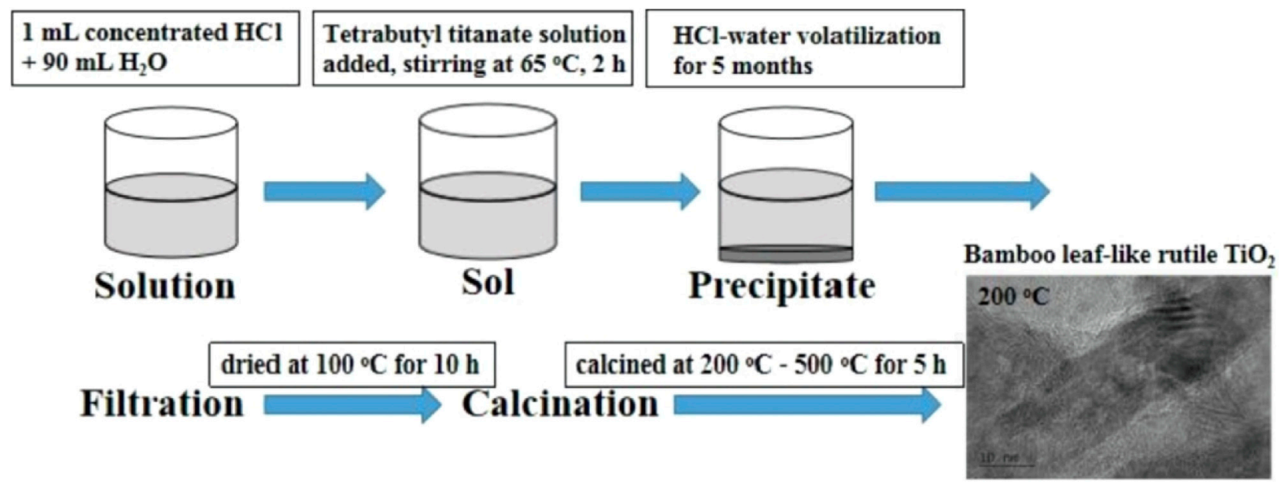

FIGURE 1 | Preparation flow chart of pure TiO_2 nanoparticles prepared by the HCl–water volatilization-assisted precipitation method. Adapted from Ren et al. (2022). Copyright © 2021 Elsevier B.V.

activity for the degradation of methyl orange. **Figure 1** shows the preparation flow chart of pure TiO_2 nanoparticles prepared by using the HCl–water volatilization-assisted precipitation method. TiO_2 nanoparticles prepared by using this method have a one-dimensional structure, which greatly enhances its specific surface area and improves its photocatalytic activity. The polyacrylamide gel method is also a common method used to prepare TiO_2 nanoparticles. The nanoparticles prepared by this method are uniformly dispersed with almost no adhesion agglomeration and are widely used in the preparation of metal oxide semiconductor materials and multiple heterojunction composite semiconductor materials (Xian et al., 2013; Gao et al., 2021a; Gao et al., 2021b; He et al., 2021b; Li et al., 2021b; Liang et al., 2021; Tang et al., 2022a; Liu et al., 2022b; Fu et al., 2022; Gao et al., 2022; Wang et al., 2022). Lu et al. (2022) prepared the TiO_2 nanotube photocatalysts, which exhibit high photocatalytic activity for the degradation of patulin in simulated juice. This special structure enables TiO_2 to achieve new applications in the degradation of cold drugs.

2.2 Preparation of Micro/Nanostructured Ion-Doped TiO_2 Photocatalysts

Ion doping mainly includes metal ion doping and non-metal ion doping. Metal ion doping mainly introduces metal ions such as alkali metals, transition metals, and rare earth metals into the crystal structure of pure TiO_2, making metal ions become the receiver pole of photogenerated electrons or the defect that can capture photogenerated electrons, thus improving the separation of the photogenerated charge carrier and correspondingly improving the photocatalytic capacity of photocatalysts. Non-metallic ion doping generally involves doping B, N, C, S, and other non-metallic elements close to O elements into TiO_2 photocatalysts. It is generally believed that the hybridization of p orbital and 2p orbital of O in the non-metal leads to an upward shift in the valence band width of TiO_2, which reduces the band gap width and enables TiO_2 to absorb visible light.

The key to the synthesis of ion-doped TiO_2 is to control the composition and content of doped ions and element substitution for the position of Ti. Researchers usually adopt physical and chemical methods to enhance the photocatalytic activity of TiO_2 by doping metal ions or non-metal ions in the lattice position of Ti or modifying the surface of TiO_2. Generally, it is easy to modify TiO_2 with metal ions, and the photocatalytic and bacteriostatic activities of TiO_2 can be greatly improved by chemical experiments. Ellouzi et al. (2021) synthesized silver-doped TiO_2 nanoparticles by the glucose-assisted ball-milling method, which exhibit high photocatalytic activity for efficient photodegradation of rhodamine B. The preparation flow chart of silver-doped TiO_2 nanoparticles prepared by using the glucose-assisted ball-milling method is shown in **Figure 2**. As can be seen from the figure, it is easier to modify Ag particles to the surface of TiO_2 nanoparticles by the glucose-assisted ball-milling method, thus improving the uniformity of the entire sample particles. Venkatachalam et al. prepared Mg^{2+}- and Ba^{2+}-doped TiO_2 nanoparticles by using the sol–gel method (Venkatachalam et al., 2007). The band gap value of nano-TiO_2 doped with Mg^{2+} and Ba^{2+} is higher than that of pure nano-TiO_2, but the photocatalytic activity of 4-chlorophenol degradation is higher than that of pure nano-TiO_2 and commercial Degussa P25. Hu et al. (2022) synthesized Ni-doped TiO_2 nanotubes by using the anodic oxidation method, which exhibit high electrocatalytic activity for the degradation of phenol wastewater. Zhou et al. (2019) prepared a photocatalyst doped with six different types of rare earth (RE) ions (La, Ce, Pr, Nd, Eu, or Gd) by using the microwave hydrothermal treatment method. The results showed that the structure and chemical properties of nanocomposites are related to the radius of Re^{3+}. Since the radius of Re^{3+} is much larger than that of Ti^{4+}, Ti^{4+} can replace Re^{3+} in the lattice of Re_2O_3 in the form of Ti^{3+}, and it produces charge imbalance due to its small ionic radius.

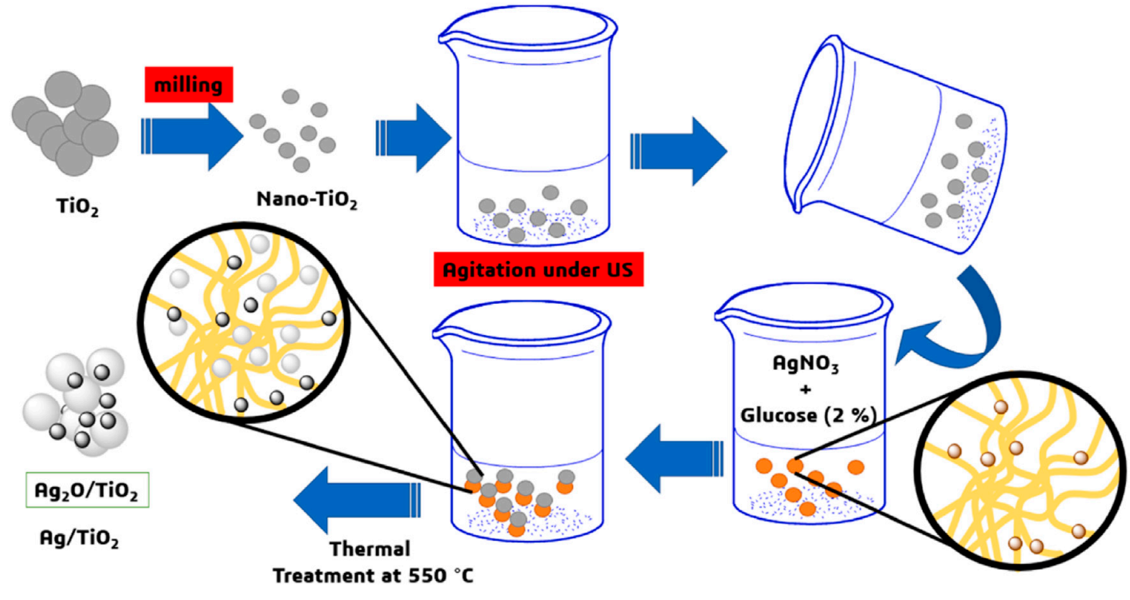

FIGURE 2 | Preparation flow chart of silver-doped TiO_2 nanoparticles prepared by the glucose-assisted ball-milling method. Adapted from Ellouzi et al. (2021).

Boningari et al. (2018) successfully prepared N-doped TiO_2 by using a new single-step flame spraying method. The results showed that the N atom is effectively doped into the crystal structure of TiO_2. The combination of the N atom and TiO_2 crystal structure changed the electronic band structure of TiO_2, formed a new middle gap energy state N 2p band in the O 2p valence band, reduced the band gap width of TiO_2, and transferred the optical absorption of TiO_2 to the visible region. The results showed that the N-doped TiO_2 improved TiO_2's solar energy utilization rate. Zhang et al. (2015) continuously deposited TiO_2 using monodispersed cationic polystyrene microspheres as templates by using the directional self-assembly method and then removed cationic polystyrene microspheres by calcination at 450°C to obtain C-doped hollow TiO_2. Under visible light irradiation, C-doped hollow anatase TiO_2 has better photocatalytic activity than commercial P25.

2.3 Preparation of Micro/Nanostructured TiO_2-Based Composite Photocatalysts

The TiO_2-based composite photocatalysts mainly show two states: one is the formation of heterojunction, and the other is mixed together in a simple way. Semiconductor heterostructures are usually constructed by coupling two or more semiconductors with different band gap widths to widen the light response range of wide-gap semiconductors and improve the separation efficiency of photogenerated electron hole pairs. If two or more semiconductor materials are simply combined, a simple one-step synthesis can be performed by many chemical processes. When two or more semiconductor materials are combined in a heterojunction, special preparation methods are required to couple them together. Some special morphologies, such as the hierarchical structure and core-shell structure, were constructed to promote the separation of photogenerated electron holes from the built-in electric field, thus improving the photocatalytic efficiency of the photocatalyst.

There are many methods for heterostructure construction, including the sol–gel method, electrostatic spinning method, hydrothermal method, solvothermal method, spin-coating method, and facile solid–liquid adsorption template technology, followed by calcination process. **Table 1** shows the preparation method of micro/nanostructured TiO_2-based composite photocatalysts. Based on the different uses of TiO_2 composite photocatalyst, different methods can be used to regulate and synthesize heterojunction composites with different morphologies. Wang et al. (2021b) prepared SiO_2-TiO_2@PDMS by the spray method, which exhibited excellent repellent effect toward organic dye droplets and good mechanical stability. Xu et al. (2022) synthesized the core-shell C@TiO_2 microspheres by using a three-step method, which exhibit high electrochemical property. **Figure 3** shows the preparation flow chart of core-shell C@TiO_2 microspheres prepared by using a three-step method. Uniform core-shell C@TiO_2 microspheres can be obtained by this method. However, in order to increase the photocatalytic or bacteriostatic activity of TiO_2-based composite photocatalysts, defects, impurity levels, and transport carrier of charge carriers should be introduced into the composite. As the companion of TiO_2 heterojunction, the selection of the other half plays a crucial role in the photocatalytic and antibacterial activities of TiO_2 catalysts. Improper selection of another semiconductor may result in the reduced photocatalytic or bacteriostatic activity of the entire system. Therefore, the

TABLE 1 | Preparation method of micro/nanostructured TiO_2-based composite photocatalysts.

Catalyst	Preparation method	Reference
MAO/TiO_2	Spin-coating method	Zhang et al. (2022)
SiO_2-TiO_2@PDMS	Spray method	Wang et al. (2021b)
Si@TiO_2/C	Facile solid–liquid adsorption template technology followed by the calcination process	Xiang et al. (2020)
Core-shell C@TiO_2	Three-step method	Xu et al. (2022)
Ag_2O/TiO_2	Two-step method	Gao and Wang, (2021)
Polymeric carbon nitride/TiO_2	Template method	Wu et al. (2022)
Black hollow TiO_2 nanotube-coated PDA@Ag_2S	Hydrothermal and *in situ* polymerization methods	Jiang et al. (2022)
rGO-ZnS-TiO_2	Ultrasonic irradiation method	Kale et al. (2020)
ZnO/TiO_2/ZrO_2	Continuous-wave laser irradiation method	Abrinaei and Aghabeygi, (2022)
TiO_2@Y_2O_3	Sol–gel method and high-temperature calcination reduction	Jiang et al. (2021)
TiO_2/g-C_3N_4	Hard template approach	Li et al. (2021c)
$Li_4Ti_5O_{12}$–TiO_2	Solvothermal technique	Santhoshkumar et al. (2022)
SiO_2/TiO_2	Facile grinding and the calcination process	Sun et al. (2020)
TiO_2/SiO_2	Facile spraying method	Wu et al. (2021)
Pt/TiO_2/γ-Al_2O_3	Electrospinning-coated $NaBH_4$ reduction method	Zhu et al. (2022a)

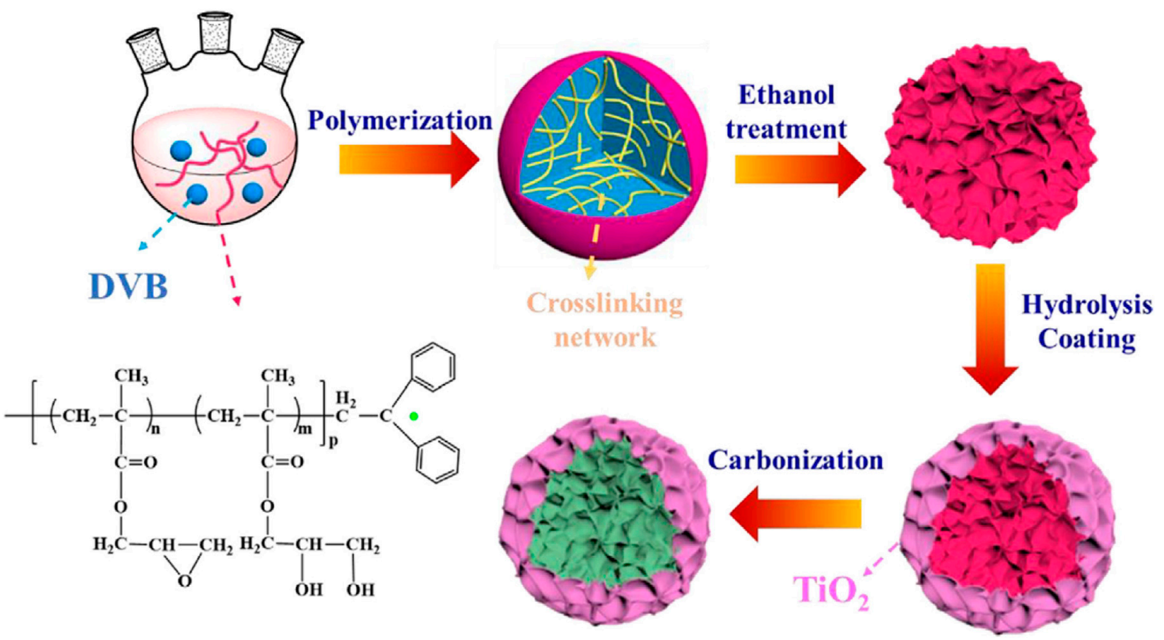

FIGURE 3 | Preparation flow chart of core-shell C@TiO_2 microspheres prepared by a three-step method. Adapted from Xu et al. (2022). Copyright © 2020 Elsevier Ltd.

preparation method is only one of the important factors affecting the photocatalytic and antibacterial activities of TiO_2-based composite photocatalysts.

3 PHOTOCATALYTIC ACTIVITY OF MICRO/NANOSTRUCTURED TiO_2-BASED PHOTOCATALYSTS

3.1 Photocatalytic Activity of Micro/Nanostructured TiO_2 Photocatalysts

The photocatalytic activity of TiO_2 strongly depends on its preparation method. TiO_2 with different morphologies can be obtained by using different preparation methods, including nanoparticles, nanoflowers, nanosheets, nanoribbons, microspheres, and nanotrees. For pure phase TiO_2, it can only respond to ultraviolet light and can degrade different kinds of dyes, drugs, and some pollutants that are difficult to degrade. Due to the small composition of ultraviolet light in natural light, this greatly limits the application of TiO_2 photocatalyst in the field of photocatalysis. The recombination rate of photogenerated carriers in TiO_2 is much higher than its mobility, which makes the photogenerated carriers to migrate to the surface of TiO_2 and participate in very few photocatalytic reactions. At present, commonly used TiO_2 photocatalysts are mainly powdered nanoparticles, which makes it difficult to separate,

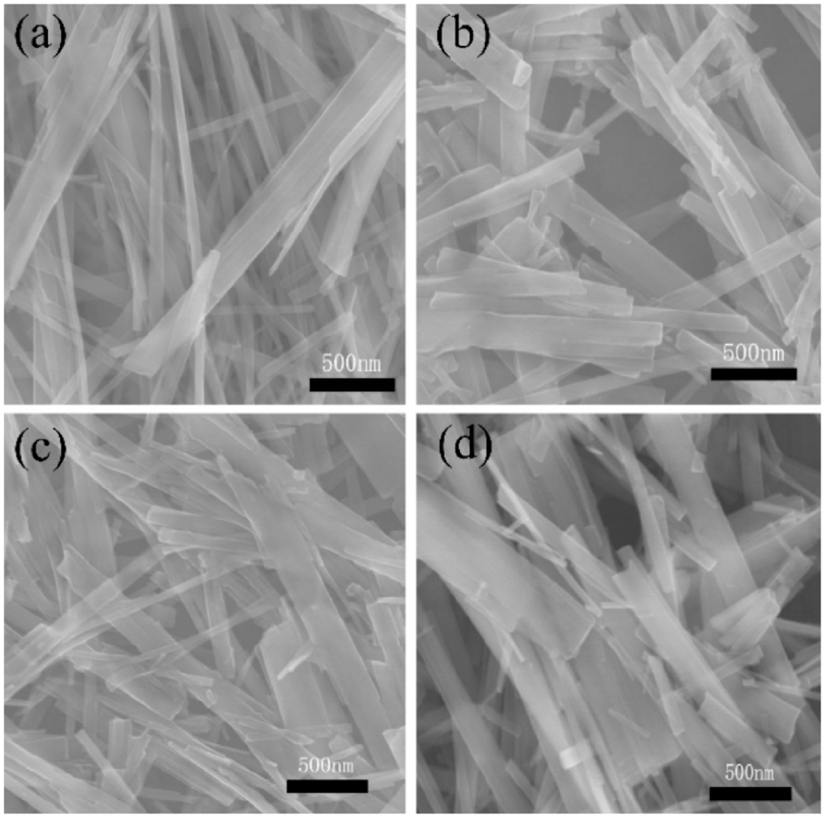

FIGURE 4 | SEM images of **(A)** TiO_2 nanobelts, **(B)** TiO_2 nanobelts calcined at 400°C for 3 h in air, **(C)** TiO_2 nanobelts with 30 mg $NaBH_4$, and **(D)** TiO2 nanobelts annealed at 400°C for 3 h under a H_2/Ar atmosphere. Adapted from Xie et al. (2021). Copyright © 2021 Capital Normal University. Published by Elsevier B.V.

recycle, and reuse from liquid after the photocatalytic reaction. On the one hand, it causes waste of photocatalysts; on the other hand, it is easy to cause secondary pollution, which limits its large-scale use. However, as a catalyst for industrial use, TiO_2 has contributed a lot.

For pure phase TiO_2 catalysts, many researchers used special preparation methods to construct defects or special morphology to enable TiO_2 to respond to visible light, thus expanding the application of TiO_2 photocatalyst in the field of photocatalysis. Xie et al. (2021) synthesized the TiO_2 nanobelts by a molten salt method with the $NaBH_4$ or H_2/Ar atmosphere and exhibits high photocatalytic activity. **Figure 4** shows the SEM images of TiO_2 nanobelts, TiO_2 nanobelts calcined at 400°C for 3 h in air, TiO_2 nanobelts with 30 mg $NaBH_4$, and TiO_2 nanobelts annealed at 400°C for 3 h under a H_2/Ar atmosphere. TiO_2 nanobelts have different concentrations of oxygen vacancies and special electronic structures through different treatment methods, thus enhancing the transfer and separation efficiency of electrons and holes in TiO_2 and finally achieving the purpose of enhancing the photocatalytic activity of TiO_2 nanoribbons. Therefore, a variety of extreme conditions are used to construct TiO_2 surface defects, regulate the electronic structure of TiO_2, and enable it to have high oxidation or reduction capacity, thus achieving the purpose of degrading dyes. However, this approach often has the disadvantages of high equipment requirements, high cost, and unsafe, and the concentration of surface defects cannot be accurately controlled, which further limits the development of this technology. Kaushik et al. (2019) transformed 2D TiO_2 to mesoporous hollow 3D TiO_2 spheres by using the solvothermal strategy followed by thermal treatment, which exhibit high photocatalytic and antibacterial activities. This strategy provides a new idea for the follow-up study of TiO_2.

3.2 Photocatalytic Activity of Micro/ Nanostructured Ion-Doped TiO_2 Photocatalysts

Ion doping is one of the effective ways to enhance the photocatalytic activity of the TiO_2 photocatalyst. The optical band gap value of TiO_2 can be effectively improved by doping different ions. The reduction of its optical band gap value enables it to respond to visible light, expanding its application in the field of photocatalysis. The ultimate goal is to prevent the recombination of electron–hole pairs inside TiO_2 so that electrons react with dyes in its conduction band, and the holes in the valence band react with dyes to generate

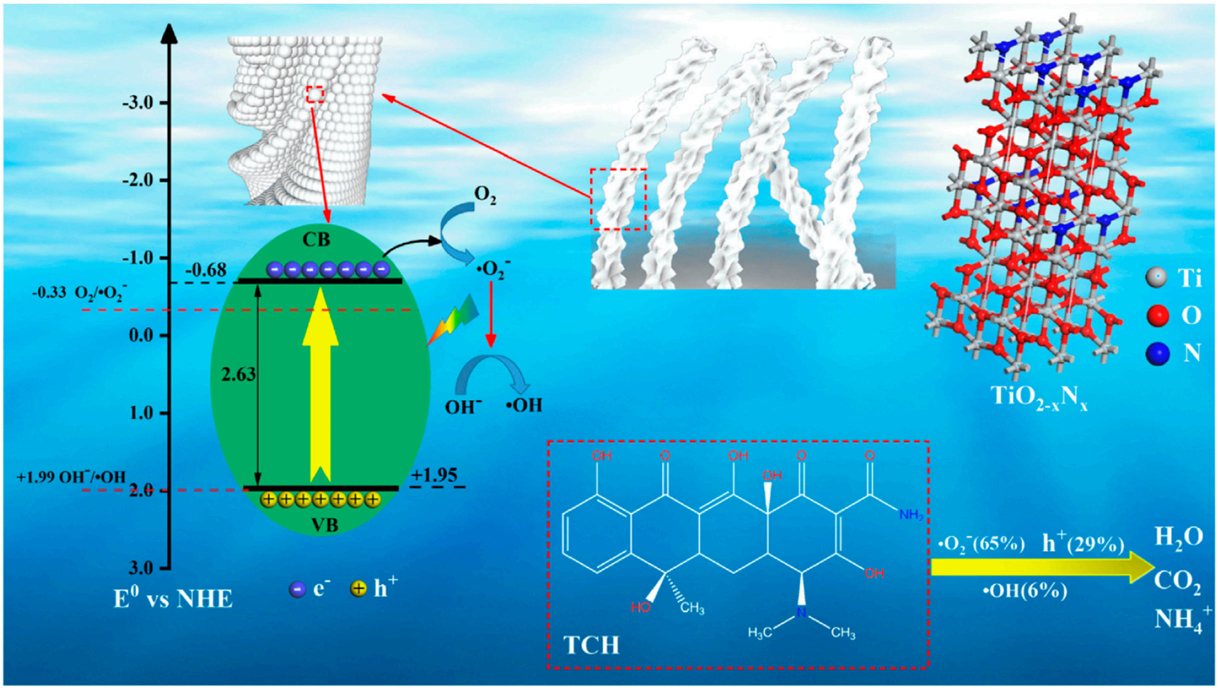

FIGURE 5 | Photocatalytic mechanism diagram of C-modified and N-doped TiO_2 photocatalysts. Adapted from Zhu et al. (2022b). Copyright © 2022 Elsevier B.V.

non-toxic and harmless products. Ion doping is divided into metal doping and non-metal doping, and metal doping is mainly performed by doping rare earth ions and transition metal ions (Santos et al., 2022). As for noble metal ions, they are easy to exist in the elemental form, so TiO_2 is mostly modified on the surface of noble metal particles to enhance the photocatalytic activity of TiO_2 (Phromma et al., 2022). The photocatalytic activity of ion-doped TiO_2 is also affected by the surface morphology, oxygen vacancy, electronic structure, and optical band gap value.

Unlike metal ion doping, non-metal ion–doped TiO_2 can be sintered at high temperature to remove non-metal ions. Therefore, it is necessary to control the appropriate sintering temperature to keep non-metal ions. This will bring a new problem: the content of non-metallic ions cannot be controlled. However, non-metallic ion doping does solve the shortcoming that TiO_2 cannot respond to visible light, which enables it to have high visible light photocatalytic activity. Zhu et al. (2022b) reported that the C-modified and N-doped TiO_2 photocatalysts prepared by the hydrothermal method using tetrabutyl titanate (TBOT) and feathers of chicken as the precursor exhibit high photocatalytic activity for the degradation of tetracycline hydrochloride under visible light irradiation. **Figure 5** shows the photocatalytic mechanism diagram of C-modified and N-doped TiO_2 photocatalysts. Carbon acts as a carrier of charge carriers in the whole system, separating photogenerated electrons and holes in space. Nitrogen doping can make TiO_2 respond to visible light.

3.3 Photocatalytic Activity of Micro/Nanostructured TiO_2-Based Composite Photocatalysts

TiO_2 composite photocatalysts can overcome the shortcoming of uncontrollable doping content of non-metal ions. Combining the advantages of two or more kinds of semiconductor materials, the whole system has physical and chemical properties that a single component does not have at the same time, which is the key to the design of TiO_2-based composite photocatalysts (Perales-Martínez et al., 2015; Hao et al., 2016; Sotelo-Vazquez et al., 2017). This design method will not only change the optical band gap value of TiO_2 but also will introduce surface defects or oxygen vacancies at the interface of the two semiconductors. Therefore, the study of the interface characteristics of two or more semiconductors is conducive to insight into the photocatalytic mechanism of TiO_2-based complex photocatalyst. In addition to metal oxides that can form heterojunctions with TiO_2, some polymers and sulfides can also form heterojunctions with TiO_2 in special ways to enhance the photocatalytic activity of TiO_2 (Vorontsov et al., 2001; Liao et al., 2010; Antoniadou et al., 2011; Riaz et al., 2015). Therefore, there are many kinds of TiO_2-based photocatalysts, but the ultimate goal is to make TiO_2

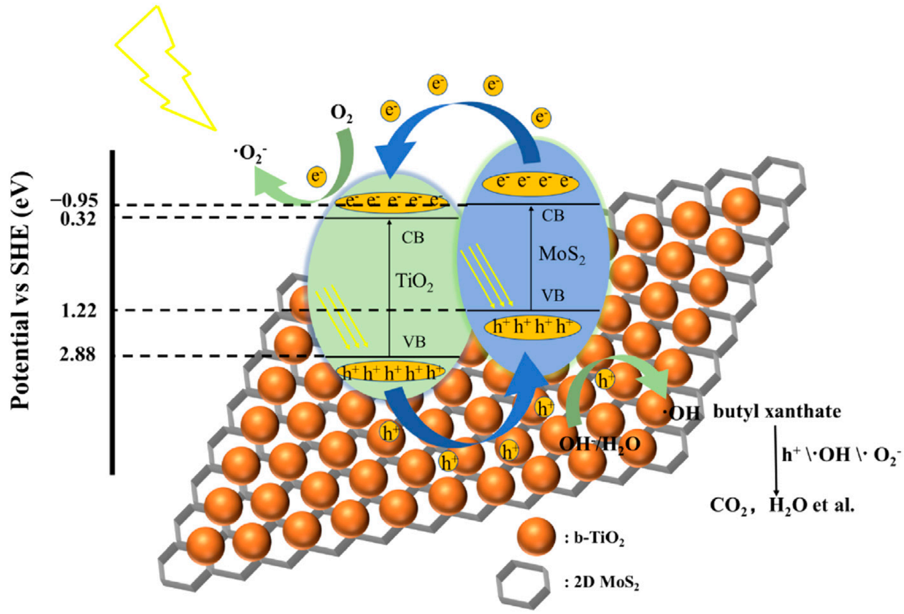

FIGURE 6 | Photocatalytic mechanism diagram of b-TiO_2 @MoS_2 photocatalysts. Adapted from Tang et al. (2022b). Copyright © 2022 Elsevier B.V.

exhibit high visible light photocatalytic activity or show new physical and chemical properties.

To summarize, there are four main ways to form a heterojunction (Schuettfort et al., 2009; Low et al., 2017; Guo et al., 2021): one is that the conduction band of a semiconductor is located in the conduction band and valence band of another semiconductor. The other is that the conduction band and valence band of one kind of semiconductor are located in the interior of another kind of semiconductor. Third, the conduction band and valence band of the two kinds of semiconductor are completely separated. Fourth, there is no conduction band and valence band between metal particles and semiconductor heterojunction. Tang et al. (2022b) reported that the b-TiO_2 @MoS_2 photocatalysts synthesized by an ultrasound technique coupled with the sol–gel method at low temperature exhibit high visible light photocatalytic activity. A photocatalytic mechanism diagram of b-TiO_2 @MoS_2 photocatalysts is shown in **Figure 6**. As can be seen from the figure, the valence band of MoS_2 is located inside the conduction band and valence band of TiO_2. Such a structure facilitates the relaxation of electrons from the more negative conduction band of MoS_2 to the conduction band of TiO_2, and the transition of holes from the more positive valence band of TiO_2 to the valence band of MoS_2, thus promoting the separation of electrons and holes. At present, the construction of special heterojunction TiO_2-based composite photocatalysts has become the most popular effective way to enhance the photocatalytic activity of TiO_2 photocatalysts.

4 ANTIBACTERIAL ACTIVITY OF MICRO/NANOSTRUCTURED TiO_2-BASED PHOTOCATALYSTS

4.1 Antibacterial Activity of Micro/Nanostructured TiO_2 Photocatalysts

The high antibacterial properties of orthopedic implants are an effective way to avoid infection during surgery, which will reduce the incidence of amputation or death due to infection. Generally, antibacterial materials can be divided into natural antibacterial materials, organic antibacterial materials, and inorganic antibacterial materials (Li et al., 2020). Inorganic antibacterial materials can be divided into two categories: one is the prepared antibacterial materials containing copper, silver, zinc, and other metal antibacterial ions; the second is photocatalytic antibacterial materials represented by TiO_2; such inorganic antibacterial materials can play an antibacterial role under the condition of ultraviolet light irradiation, water, or oxygen (Chen et al., 2017; Wang et al., 2020c). TiO_2 is a widely studied orthopedic implant material with high photocatalytic antibacterial activity. Titanium dioxide has become the most common photocatalytic antibacterial material because of its low toxicity, high safety, and no irritation to skin. Silver antibacterial materials take about 24 h to exert the antibacterial effect, while the oxide ingots only take about an hour. Moreover, the antibacterial effect of the dioxide ingot is carried out through photocatalysis, and it itself will not be consumed in the antibacterial process so that the antibacterial material of dioxide ingot has a more lasting antibacterial performance.

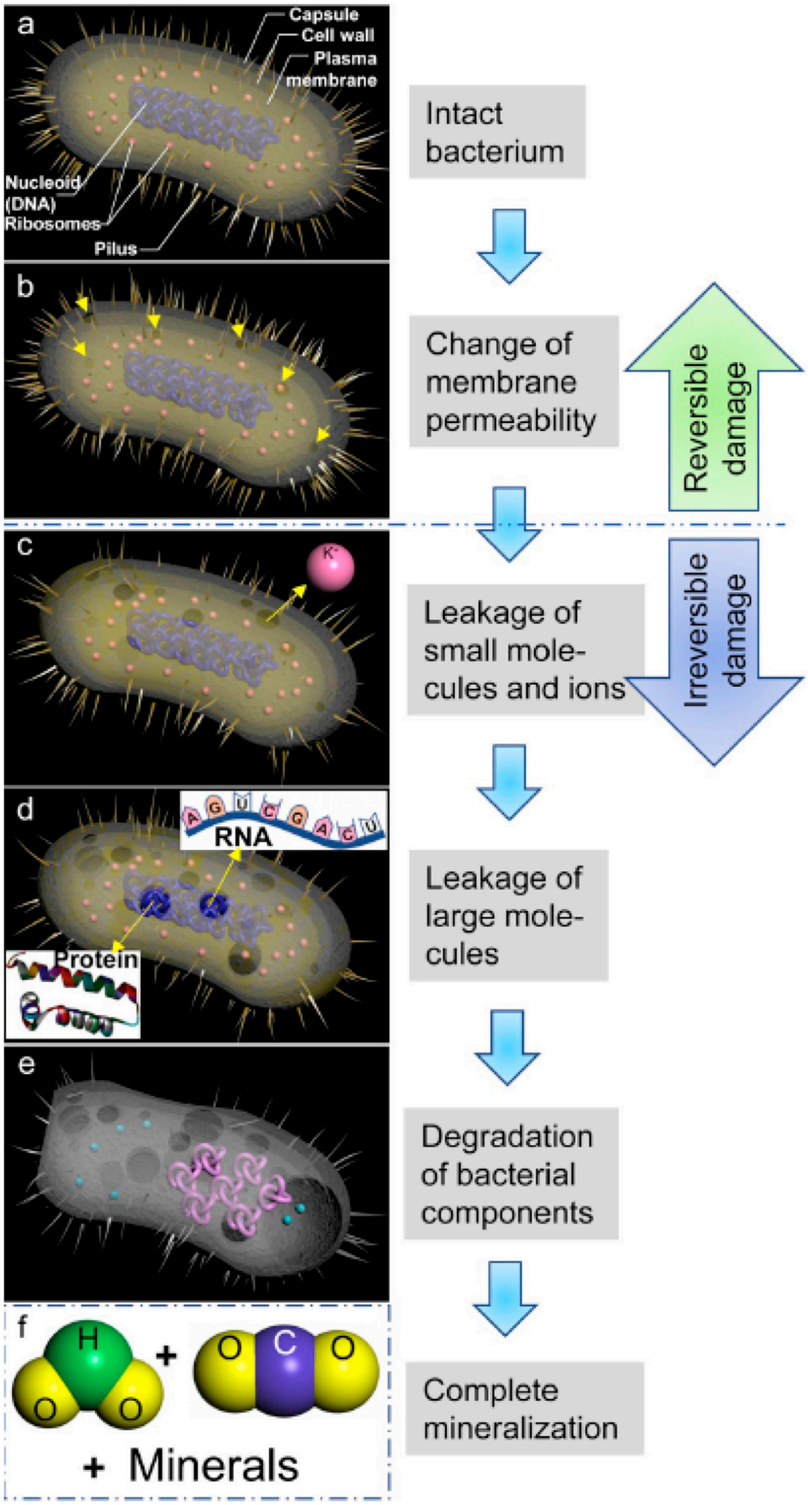

FIGURE 7 | Photocatalytic bactericidal process of TiO_2 photocatalysts. Adapted from Ge et al. (2019). Copyright © 2020 Production and hosting by Elsevier B.V. **(A)** An intact bacterium; **(B)** Bacterial oxidized by TiO_2 photocatalysis; **(C)** The bacterium leak small molecules and ions; **(D)** Leakage of higher molecular weight components; **(E)** Degradation of bacterial internal components; **(F)** The bacterium was completely mineralized.

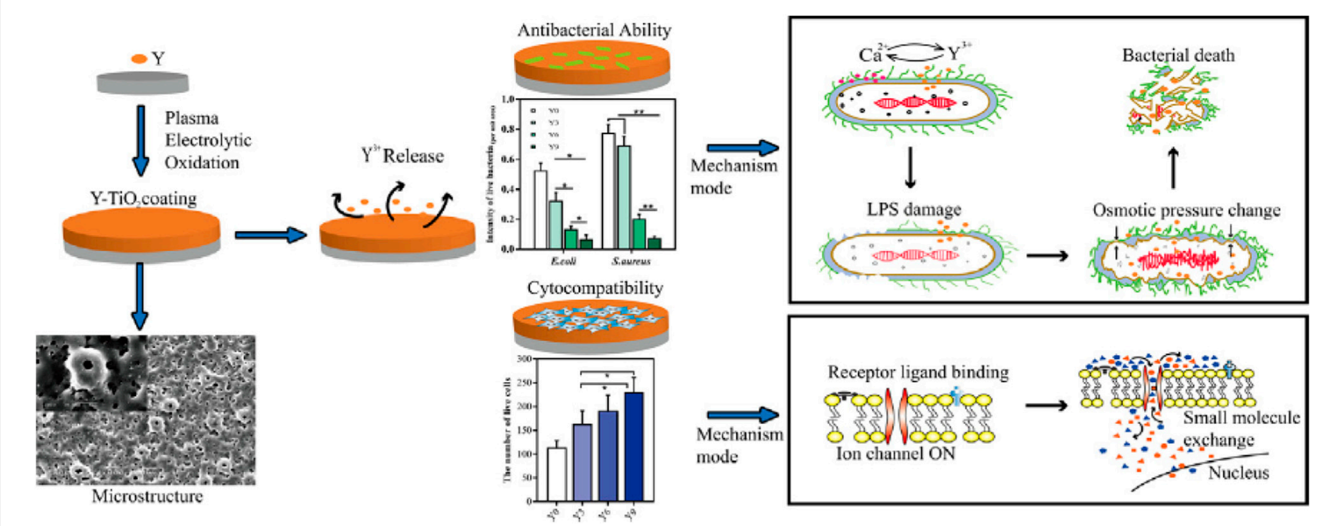

FIGURE 8 | Preparation flow chart and antibacterial mechanism of Y-doped TiO_2 photocatalysts. Adapted from Zhang et al. (2020). Copyright © 2020 Published by Elsevier Ltd.

The antibacterial mechanism of titanium dioxide is similar to its photocatalytic mechanism, and the resulting hydroxyl radicals can react with biological macromolecules, damage the structure of biological cells, and then lead to cell death. **Figure 7** shows the photocatalytic bactericidal process of TiO_2 photocatalysts. Bacteria eventually mineralize H_2O, CO_2, and other small molecular organics under the action of TiO_2 (Ge et al., 2019). Similarly, the antibacterial activity of TiO_2 is affected by its morphology, surface defects, oxygen vacancy concentration, and electronic structure (Mazare et al., 2016). At the same time, the crystal type of titanium dioxide also has a great influence on its antibacterial activity. TiO_2 has high antibacterial activity under ultraviolet light irradiation, but TiO_2 is powerless under visible light irradiation due to the limitation of its own optical band gap value. Therefore, researchers are committed to improving the photocatalytic antibacterial mechanism of TiO_2 through ion doping and heterostructure construction.

4.2 Antibacterial Activity of Micro/Nanostructured Ion-Doped TiO_2 Photocatalysts

In the process of using the antibacterial activity of titanium dioxide, the photoresponse range of titanium dioxide is narrow, and the photoelectron–hole pair is easy to compound. To solve such problems, TiO_2 photocatalytic materials can be modified structurally or on the surface so as to increase the light response range. This modification process can also reduce the recombination probability of carriers and improve the quantum efficiency, thus enhancing the photocatalytic bacteriostatic effect of TiO_2. Recently, the application of TiO_2 in the field of antibacterial materials has achieved remarkable results. With the continuous development and utilization of antibacterial performance of the TiO_2 photocatalyst, glass, ceramics, metal products, coatings, fibers, plastics, and other antibacterial products can be produced by plating on the surface of materials or doping in other materials (Mori, 2005; Tung and Daoud, 2011).

Ion-doped TiO_2 photocatalysts have been widely used in the bacteriostatic field. Similar to the photocatalytic activity of the TiO_2 photocatalyst, ion-doped TiO_2 can be divided into metal ion doping and non-metal ion doping when studying the antibacterial activity of ion-doped TiO_2. Zhang et al. (2020) reported that the Y-doped TiO_2 photocatalysts prepared by the plasma electrolytic oxidation method exhibit high bacteriostatic activity. **Figure 8** shows the preparation flow chart and antibacterial mechanism of Y-doped TiO_2 photocatalysts. The result shows that the Y-doped TiO_2 photocatalysts possess excellent bacteriostatic activity against *Staphylococcus aureus* and *Escherichia coli* and outstanding biocompatibility and antibacterial capacity. Yadav et al. (2014) prepared nickel-doped TiO_2 nanoparticles by using the sol–gel method, which show the high photocatalytic inactivation and lower recombination rate of photogenerated charge carriers. Similarly, non-metallic doping can also greatly improve the antibacterial activity of TiO_2. Cao et al. (2014) reported that the N-doped TiO_2 thin films coated on stainless steel brackets exhibit high antibacterial activity against *Lactobacillus acidophilus* and *Candida albicans*.

4.3 Antibacterial Activity of Micro/Nanostructured TiO_2-Based Composite Photocatalysts

The construction of heterojunction will greatly improve the surface oxygen vacancy concentration and interface

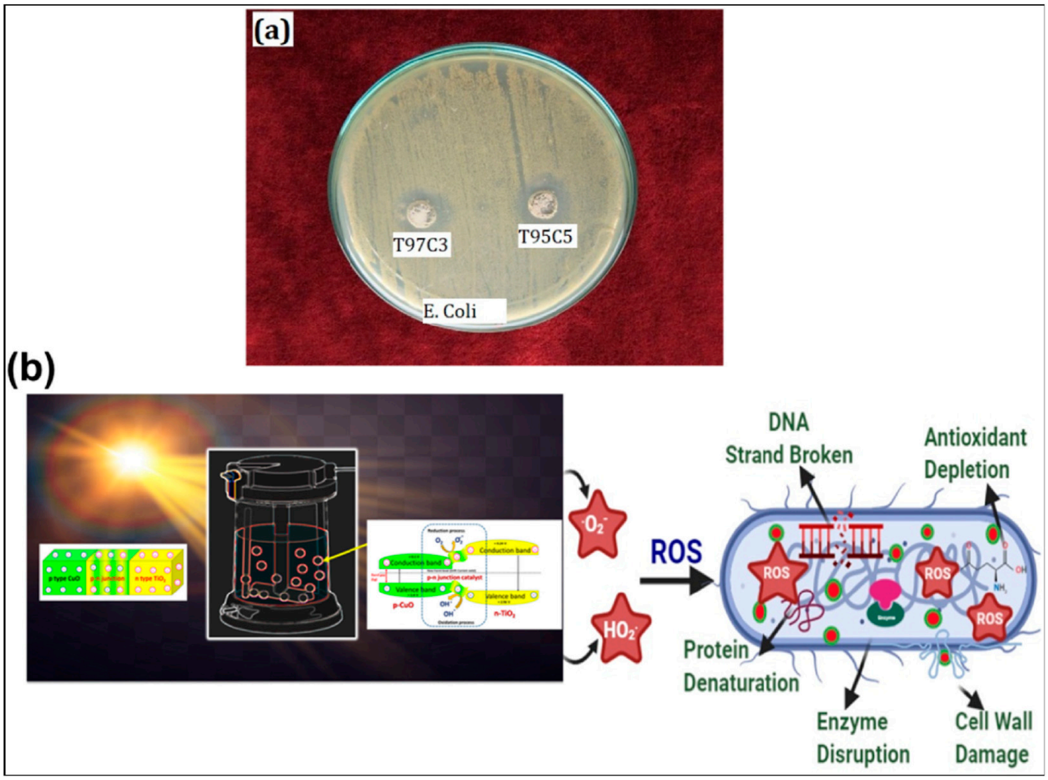

FIGURE 9 | (A) Antibacterial activity and **(B)** antibacterial mechanism of the p-n junction TiO_2/CuO heterojunction composite photocatalysts. Adapted from Gnanasekaran et al. (2021). Copyright © 2021 Elsevier Ltd.

characteristics of TiO_2 so that it has a high antibacterial activity and a potential application prospect in orthopedic implants. Similar to the study on the photocatalytic activity of TiO_2, its antibacterial activity has received unprecedented attention. The construction of heterojunction can form microspheres, mesoporous structures, layered structures, nanotubes, nanosheets, nanoribbons, nanotrees, and various flower-like structures (Wu et al., 2014; Lou et al., 2019; Murthy, 2019). These special morphologies will make TiO_2-based composite photocatalysts have high antibacterial activity. Combining the advantages of a variety of semiconductors will expand the application of TiO_2 in different fields, which is the absolute advantage of heterogeneous structure construction (Ma et al., 2015). Therefore, TiO_2-based heterojunction composite photocatalysts are widely favored by researchers.

Gnanasekaran et al. (2021) reported that p-n junction TiO_2/CuO heterojunction composite photocatalysts synthesized by the sol–gel method, followed by chemical precipitation methods, exhibit high photocatalytic and antibacterial activities. **Figure 9A** shows the antibacterial activity of p-n junction TiO_2/CuO heterojunction composite photocatalysts. The results indicate that the p-n junction TiO_2/CuO heterojunction composite photocatalysts possess high bacteriostatic activity. The antibacterial mechanism of the p-n junction TiO_2/CuO heterojunction composite photocatalysts is shown in **Figure 9B**. The conduction band and valence band of CuO are completely located inside TiO_2. However, due to the spatial separation of charge carriers, CuO and CuO have high transfer and separation efficiency, thus enhancing the antibacterial activity of TiO_2. At present, researchers focus on how to apply the prepared TiO_2-based heterojunction composite photocatalysts to orthopedic implants, hoping to move the research of TiO_2 from laboratory to practical application.

5 TIO_2-BASED PHOTOCATALYSTS FOR APPLICATION IN ORTHOPEDIC IMPLANTS

5.1 TiO_2 Photocatalysts for Application in Orthopedic Implants

Biomaterials implanted in the body will induce a series of reactions, including postoperative infection, inflammatory reaction (acute inflammatory reaction and chronic inflammatory reaction), and fibrous tissue hyperplasia, which can prolong the treatment period and increase the treatment cost of patients at one level or lead to amputation or even death of patients due to infection (Anderson, 1993; Lin et al., 2014; Zhang et al., 2021). The mechanism of infection around orthopedic implants is that bacteria adhere to the implant surface and form

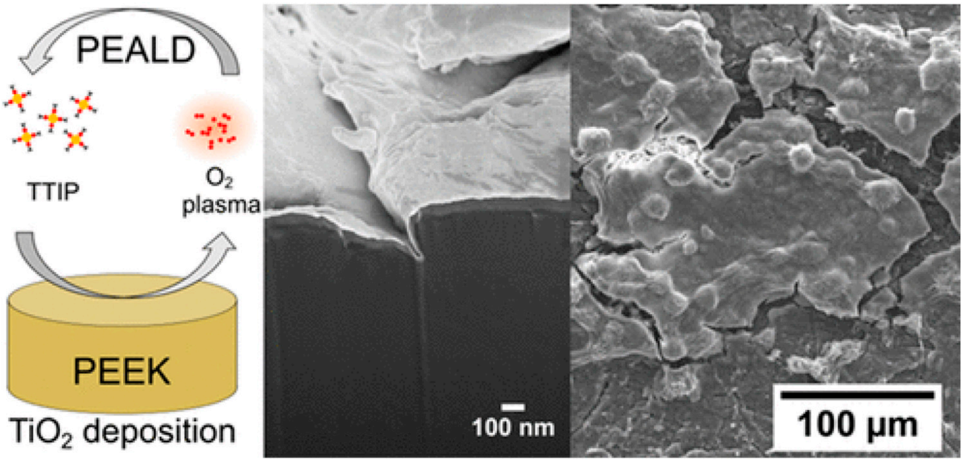

FIGURE 10 | Deposition mechanism and SEM images of TiO_2 thin films. Adapted from Blendinger et al. (2021). Copyright © 2021 The Authors. Published by the American Chemical Society.

biofilms. Deposition, adhesion, and growth are three main processes of biofilm formation. Therefore, orthopedic implants need to have high biocompatibility and bacteriostatic activity. TiO_2 has low toxicity, high biocompatibility, and high bacteriostatic activity, so it can be used as orthopedic implants in the medical field.

Blendinger et al. (2021) deposited TiO_2 thin films on the orthopedic implant material polyetheretherketone (PEEK) by plasma enhanced atomic layer deposition, which exhibit high biocompatibility and osteogenic properties. **Figure 10** shows the deposition mechanism and SEM images of TiO_2 thin films. This method provides a new idea for studying the biocompatibility and bacteriostatic properties of TiO_2 orthopedic implants. Antibiotics such as vancomycin, gentamicin, amoxicillin, and berberine were used in the study of pit bacteria coating on the titanium implant surface, among which gentamicin and vancomycin were the most commonly used. Popat et al. (2007) prepared TiO_2 nanotubes by using the anodic oxidation method and then loaded gentamicin into TiO_2 nanotubes. Experimental results showed that the gentamicin-loaded TiO_2 nanotubes could inhibit bacterial reproduction with good biocompatibility, but the release of antibiotics was faster. Due to the limitation of physical and chemical properties of pure TiO_2, its application in orthopedic implants is limited. In order to break through this limitation, ion doping and heterostructure construction are necessary effective methods to expand the application of TiO_2 in orthopedic implants.

5.2 Ion-Doped TiO_2 Photocatalysts for Application in Orthopedic Implants

In antibacterial agents, silver antibacterial agents have a wide range of antibacterial ability; can fight against Gram-negative bacteria, fungi, and even viruses; have low cytotoxicity, good stability, and low effective concentration; and are not easy to produce drug resistance and other advantages. Compared with eukaryotic cells, silver has greater toxicity to prokaryotic cells, so silver has excellent inhibition of microbial growth and proliferation and low cytotoxicity to biological somatic cells. Nanoscale silver particles have a high specific surface area, high contact probability with bacteria, and strong chemical activity. Atoms on the surface of silver particles are easy to bond with other chemical groups, and their antibacterial effect is much stronger than that of micron silver particles. Therefore, Ag-doped TiO_2 can improve the antibacterial activity and biocompatibility of TiO_2, which can be used in orthopedic implants. Zhao et al. (2013) used the anodic oxidation method and hydrothermal method in titanium implant surface preparation of Ag- and Sr-doped TiO_2 nanotubes, by changing the process parameters for different structures of TiO_2 nanotubes, as well as the precursor concentration change of Ag and Sr, and antibacterial performance and characterization of the biological activity of TiO_2 was improved. According to the results, TiO_2 coatings doped with Ag and Sr have good antibacterial activity and cytocompatibility. Amin Yavari et al. (2016) prepared TiO_2 nanotubes on the surface of 3D-printed porous titanium, then loaded the nanotubes with Ag nanoparticles, obtained a composite coating loaded with silver antibacterial factors on the surface of porous titanium, and studied the killing ability of silver ions on *Staphylococcus aureus*.

Lv et al. (2021) reported that the Zn-modified TiO_2 photocatalysts prepared by the micro-arc oxidation technique exhibit high cytocompatibility and bactericidal ability for orthopedic implants. **Figure 11** shows the pathological photographs of Zn-modified TiO_2 photocatalysts. The result indicates that the Zn-modified TiO_2 coating produced by the micro-arc oxidation technique benefits the application in the orthopedic implanted devices. Due to technical limitations, ion-doped TiO_2 is rarely used in orthopedic implants. At the same time, this is due to the fact that simple particles in the air are easy to be oxidized or easy to dissolve in water solution and release

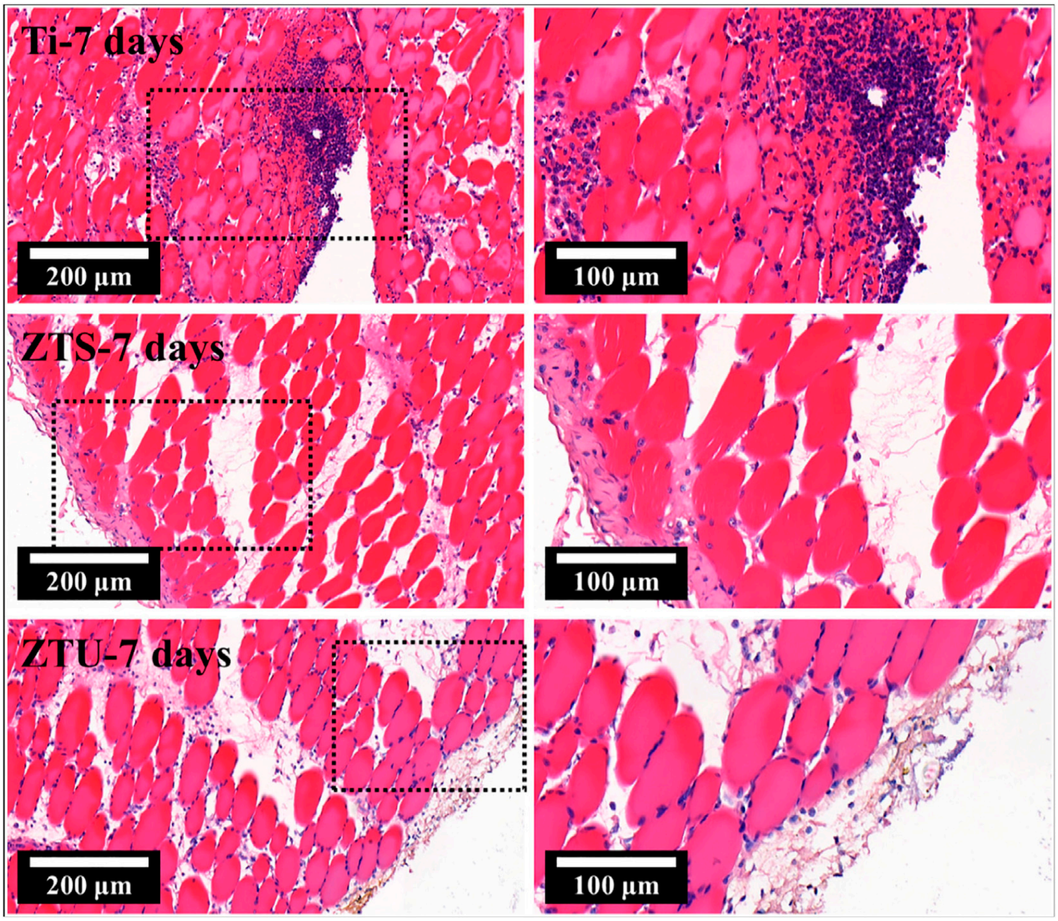

FIGURE 11 | Pathological photographs of Zn-modified TiO_2 photocatalysts. Adapted from Lv et al. (2021). Copyright © 2021 Elsevier B.V.

metal ions, resulting in high concentration of silver ions and fine toxicity. The aforementioned problems also occur when the elemental particles are combined or doped with TiO_2, thus limiting the application of ion-doped TiO_2 photocatalysts in orthopedic implants.

5.3 TiO_2-Based Composite Photocatalysts for Application in Orthopedic Implants

In order to overcome two or many kinds of antibacterial materials used alone, materials with excellent antibacterial properties, by putting other excellent antibacterial materials and two titanic oxide composite photocatalytic antibacterial materials, not only make it photocatalytic and antibacterial under strong light conditions but also in the dark under the condition of using other antibacterial effects of antibacterial materials (Etacheri et al., 2013; Sood et al., 2016; Mousa et al., 2021). The synergistic antibacterial effect of inorganic antibacterial materials was obtained. On the other hand, compared with traditional linear, blocky, spherical and tubular materials, multistage structural materials have better antibacterial effect because of their close contact with cells. The construction of multiple heterojunction TiO_2 composite photocatalysts can be effectively applied in the field of orthopedic implants.

Vandana et al. (2021) reported that the TiO_2-Nb_2O_5 nanoporous mixed metal oxide bone implant materials were assessed by using *in vitro* and *in vivo* methods and exhibit high biocompatibility. The result indicates that the TiO_2-Nb_2O_5 nanoporous mixed metal oxide bone implant materials are non-cytotoxic, non-hemolytic, and biocompatible. **Figure 12** shows the orthopedic applications for the TiO_2-Nb_2O_5 nanoporous mixed metal oxide bone implant materials. The results suggesting that the TiO_2-Nb_2O_5 nanoporous mixed metal oxide bone implant materials can be used safely for orthopedic applications. A variety of heterojunction composite TiO_2-based photocatalysts are widely used in the field of orthopedic implants. Therefore, its research is a very popular topic but also a fruitful topic. With the development of science and technology, the application of TiO_2-based composite photocatalysts in orthopedic implants will develop rapidly.

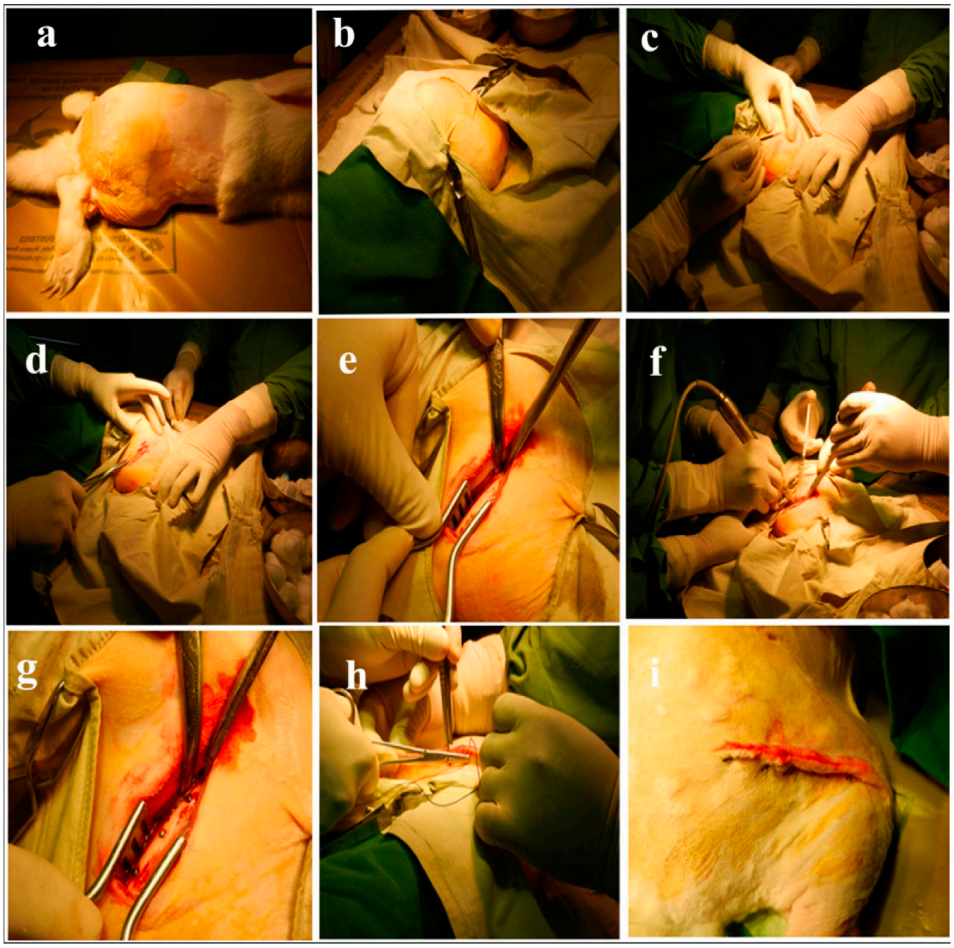

FIGURE 12 | Orthopedic applications for the TiO_2-Nb_2O_5 nanoporous mixed metal oxide bone implant materials. Adapted from Vandana et al. (2021). Copyright © 2020 Elsevier B.V. **(A, B)** Animals that lie on their side, **(C, D)** The exposed femoral cortex, **(E)** Three holes spaced 1 cm apart, **(F, G)** Material implanted, **(H, I)** Suture with sterile stitches.

6 CONCLUSION AND OUTLOOK

6.1 Conclusion

TiO_2 with three crystal structures has the characteristics of non-toxic and excellent physical and chemical properties and has been applied in many fields. Due to the large optical band gap value of TiO_2 and the influence of its particle size, crystal structure, and crystal defect on the photocatalytic and antibacterial activities of TiO_2, research of single-component TiO_2 in photocatalytic and medical fields is greatly limited. Therefore, using special means to develop metal ion–doped and non-metal ion–doped TiO_2 photocatalysts can expand the light response range of TiO_2 so that TiO_2 has an important application in the field of photocatalysis and bacteriostatic activities. Meanwhile, the development of heterojunction TiO_2-based composite photocatalysts can overcome the shortcomings of non-metal ion–doped TiO_2 and obtain novel physical and chemical properties so that the heterojunction TiO_2-based composite photocatalyst has broad application prospects in a variety of fields. It is worth noting that TiO_2, ion-doped TiO_2, and heterojunction TiO_2-based composite photocatalysts have low toxicity, high biocompatibility, high photocatalytic activity, and antibacterial activity, enabling them with unprecedented applications in orthopedic implants. Although TiO_2 and TiO_2-based photocatalysts have been widely used in the fields of photocatalysis and antibacterial and orthopedic implants, related technologies are still developing, which makes them have potential application prospects in many fields.

6.2 Outlook

The shortcomings of TiO_2 and TiO_2-based photocatalysts are being overcome by researchers, which have been applied in various fields. Nevertheless, there are still many topics worthy of study in the fields of photocatalysis, bacteriostasis, and orthopedic implants. 1) With the continuous development of science and technology, people are not only satisfied with the use of TiO_2 and TiO_2-based photocatalysts to degrade organic dyes but also toward more complex fields such as insoluble and difficult-to-degrade pollutants and drug degradation. 2) To develop special preparation methods to synthesize TiO_2 and TiO_2-based photocatalysts with a special defective structure and improve the application of the catalyst in the fields of photocatalysis, bacteriostasis, and orthopedic implants. 3) The TiO_2-based photocatalyst combines excellent optical, magnetic, mechanical, and electrical properties of semiconductor materials and makes the properties of the system with special optical, magnetic, mechanical, or electrical properties and the internal connection mechanism of photocatalytic and bacteriostatic activities and aforementioned properties a topic worth studying. 4) The combination of ion-doped TiO_2 and heterojunction TiO_2-based composite photocatalysts will produce new physical and chemical properties, which is also a topic worthy of study.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.