

Photocatalytic Degradation Based on Titanium Dioxide Nanoparticles as The Matrix

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Abstract. The accelerating pace of industrialization has led to escalating water pollution worldwide. Titanium dioxide nanoparticles, as a semiconductor with outstanding photocatalytic properties, hold significant value in photocatalytic degradation of organic pollutants in water. This article focuses on the improvement of the photocatalytic performance of titanium dioxide nanoparticles by doping inorganic metal and inorganic non-metal elements and preparing titanium dioxide nanoparticles from biological precursors. By comprehensively comparing the differences in band gap changes induced by different doping elements, it is found that the correct morphology and purity of the titanium dioxide nanoparticles are even more crucial for the preparation method. Therefore, this paper suggests changing the morphology of titanium dioxide nanoparticles themselves in addition to changing the doping elements, as well as co-doping inorganic metallic elements with inorganic non-metallic elements or improving the spatial three-dimensional structure. In addition, the green synthesis of titanium dioxide nanoparticles or the construction of metal-organic frameworks with organic ligands and composite inorganic semiconductors doped with Co is also a way to improve the photocatalytic efficiency of titanium dioxide nanoparticles, which points to the direction for future researchers.

Keywords: Titanium dioxide nanoparticles, Organic matter, Dope.

1. Introduction

Water is the source of life and the foundation for the survival of living activities. However, with the continuous development of industrialization, by-products and pollutants from industrial emissions have exacerbated water pollution. This includes toxic and harmful inorganic elements, as well as organic elements resulting from pigments, dyes, cosmetics, and the production processes of biological products [1]. The discharge of these toxic and harmful elements leads to increased water pollution, disrupts ecological balance, and affects human health. Therefore, the degradation of these elements has become a very important issue.

For water pollution, the methods for degrading organic and inorganic pollutants are diverse, with redox reactions, electrochemical reactions, thermal decomposition, and photocatalytic decomposition being the most common treatment methods. In recent years, photocatalytic decomposition of water pollution has garnered widespread attention due to its good economic benefits and environmental friendliness. Consequently, many photocatalysts have been experimentally tested and their photocatalytic performance compared laterally. Titanium dioxide nanoparticles are a special type of nanomaterial with excellent photocatalytic properties [1].

Titanium dioxide nanoparticles are nanoscale particles with a particle size ranging from 1 to 100 nm [2]. Due to their unique particle size distribution, they have significant applications in optics, magnetism, and other fields [2]. In recent years, the use of titanium dioxide as a matrix, combined with inorganic metal or inorganic non-metal elements and organic substances for the photocatalytic degradation of organic waste, has become increasingly popular. Various treatment methods have emerged to address different types of organic waste, with the doping of inorganic metal elements, particularly iron, being the most popular and effective. As a kind of metal oxide semiconductor nanoparticles, the energy provided by titanium dioxide nanoparticles to photocatalysis mainly comes from the valence band electron transition caused by sunlight irradiation, so titanium dioxide nanoparticles are faced with the problems of too large band gap energy value and too high electron-hole recombination rate, resulting in low photocatalytic efficiency [3]. The efforts of researchers in

recent years have also reduced the band gap width and electron-hole recombination rate of titanium dioxide so as to improve photocatalytic efficiency. This paper will start from these two issues, analyze the papers about reducing the band gap energy and electron-hole recombination rate of titanium dioxide nanoparticles in the past three years, classify the types of materials to improve the photocatalytic performance of titanium dioxide nanoparticles, summarize the effectiveness and measures that can be taken for different organic wastes to compound different elements, and provide help for subsequent researchers.

2. Photocatalytic Degradation Process of Titanium Dioxide Nanoparticles

Titanium dioxide nanoparticles, as metal oxide semiconductors, function to convert light energy into chemical energy. As shown in Figure 1, the bandgap is located between the valence band and the conduction band. Only when the energy emitted by sunlight is greater than the bandgap energy can the electrons in the valence band acquire sufficient energy (greater than the bandgap energy). The electrons in the valence band will then transition to the conduction band, creating holes in the valence band and electrons in the conduction band. The holes in the valence band (h_{VB}^+) react with water molecules to produce hydrogen gas and highly energetic hydroxyl radicals. The electrons in the conduction band (e_{CB}^-) react with oxygen and hydrogen ions in the water medium to form hydrogen peroxide. Under light conditions, hydrogen peroxide is easily decomposed into hydroxide ions and hydroxyl radicals [4]. These hydroxyl radicals, along with h_{VB}^+ and e_{CB}^- , can chemically react with organic pollutants, ultimately forming hydrocarbons as shown in Figure 1.

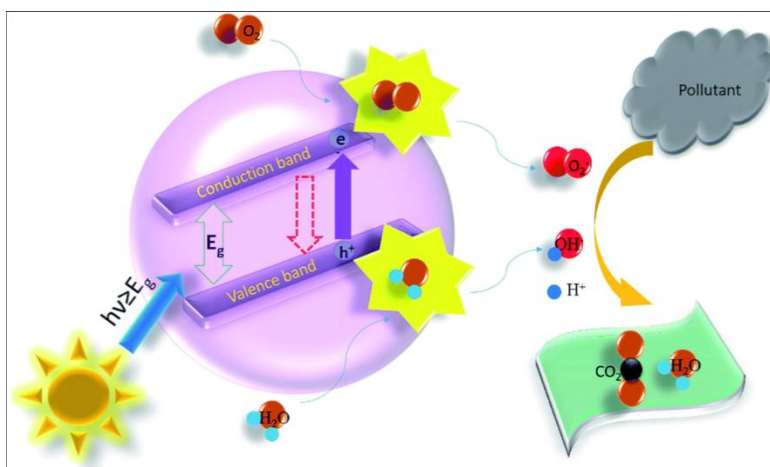


Figure 1. The idea of degradation of pollutants by heterogeneous photocatalysis [4]

For titanium dioxide nanoparticles, the limitation on their photocatalytic degradation of pollutants mainly comes from (1) the relatively wide bandgap of titanium dioxide nanoparticles, which is 3.26 eV [5]. According to Planck's equation:

$$E \cdot \lambda = 1240 \text{ (eV} \cdot \text{nm)}. \quad (1)$$

Therefore, the wavelength of light required to successfully excite titanium dioxide nanoparticles should be less than 387nm. Among the light spectrum, only ultraviolet light meets this requirement. Thus, without doping other elements to reduce the bandgap of titanium dioxide nanoparticles, ultraviolet light is one of the essential factors for initiating photocatalytic degradation. (2) Titanium dioxide nanoparticles have a relatively high electron-hole recombination rate, which is unavoidable in semiconductors. However, electrons and holes are crucial factors in whether photocatalytic reactions can proceed smoothly. To enhance the efficiency of photocatalytic degradation, it is very important to reduce the electron-hole recombination rate. The treatment of different organic pollutants, such as phenol, methylene orange, methylene blue, etc., can greatly affect the overall efficiency of photocatalysis due to their different types, pH values and even concentrations [5]. Therefore, this paper emphasizes that the photocatalytic degradation performance of organic pollutants should be

synergistically compared under various factors, and the photocatalytic degradation performance of different organic pollutants should not be compared individually.

3. Comparison of the Enhanced Degradation Performance of Inorganic-Doped Titanium Dioxide Nanoparticles

Inorganic doping of titanium dioxide nanoparticles can be categorized into two main types: metal and non-metal elements. Non-metal dopants include carbon (C), nitrogen (N), sulfur (S), boron (B), and graphene, among others [6]. Among them, carbon and nitrogen are the most widely used. Carbon has various nanostructures at the nanoscale, and nanostructures of different dimensions have different properties, which can also produce different photocatalytic characteristics for the overall components doped into titanium dioxide nanoparticles. Therefore, for the doping of inorganic non-metallic elements, people are also trying to co-operate with different inorganic non-metallic elements to improve the photocatalytic performance of components. Among metal dopants, Fe^{3+} is the most widely used. In recent years, examples of co-doping with multiple inorganic metal elements and hollow morphology Fe^{3+} -doped titanium dioxide nanoparticles have also been proposed based on Fe^{3+} doping [7]. This doping of various elements has greatly reduced the bandgap width and the wavelength range of light absorption in titanium dioxide nanoparticles. Next, this paper will focus on examples from recent years where doping titanium dioxide nanoparticles has improved their photocatalytic degradation performance and analyze their advantages and disadvantages.

3.1. Inorganic Metal-doped Titanium Dioxide Nanoparticles

When doping titanium dioxide nanoparticles with metal elements, it is important to ensure that the dopant elements have ionic radii similar to that of Ti^{4+} . Liu pointed out in the paper that when iron enters the titanium dioxide nanoparticles lattice in ionic form, the crystal appears in a clustered state [7]. At $n(\text{Fe}^{3+}):n(\text{TiO}_2) = 0.2\%$, the best photocatalytic degradation performance for the azo dye methyl orange (MO) was observed. Additionally, due to the doping of iron, the band gap energy of the semiconductor after doping was 3.17 eV. The data indicates that under the same light wavelength, the photocatalytic efficiency of TiO_2 doped with 0.2% FeCl_3 was maximally improved by 4.2 times compared to pure TiO_2 [8]. Regarding inorganic metal doping, Thambiliyagodage and others have also proposed co-doping Fe and Cu into titanium dioxide nanoparticles to deal with methylene blue. When Fe is doped into the titanium dioxide lattice, the formation of Fe^{3+} and Ti^{3+} elements after doping creates a new impurity energy level below the conduction band. This is also the reason why iron doping leads to a reduction in the band gap energy of titanium dioxide. As a transition metal, copper has a significant difference in ionic radius between Cu^{2+} and Ti^{4+} , and the introduction of foreign atoms leads to the formation of oxygen vacancies, which in turn reduces the bandgap energy of titanium dioxide nanoparticles. For titanium dioxide nanoparticles with a doping ratio of $n(\text{Fe}^{3+}):n(\text{Cu}^{2+}):n(\text{TiO}_2) = 2.5\%:7.5\%:1$, the bandgap energy is only 2.75 eV [9]. Far less than the band gap energy reduction achieved by single doping with iron, however, the photocatalytic activity of this co-doped final product is not higher than that of pure titanium dioxide nanoparticles, which is considered to be a shielding effect of one metal element on another [9](See Table 1).

3.2. Inorganic non-metal-doped Titanium Dioxide Nanoparticles

Doping carbon materials into titanium dioxide nanoparticles is an important development direction, due to the diverse morphologies of carbon allotropes and the varying properties of the carbon elements produced from different allotropes. Titanium dioxide nanoparticles were synthesized using the Sol-Gel method and then doped with poly (diallyl dimethylammonium chloride) (PDADMAC) as a carbon precursor. Studies have shown that the bandgap energy of the final material was reduced to 2.37 eV [6]. Nitrogen is the most widely used element for doping TiO_2 nanoparticles in inorganic non-metallic materials. This method can introduce a new impurity energy level in the valence band, thereby significantly reducing the band gap of TiO_2 nanoparticles. Moreover, the composite method

of N/ TiO₂ nanotubes has the highest photocatalytic degradation rate for methyl orange, where nitrogen is doped in the form of urea, and the doping ratio of urea to TiO₂ nanotubes is 1:1 [6]. Table 1 summarizes the band gap changes of pure TiO₂ nanoparticles modified by inorganic metal and non-metal materials.

Similar to metal element doping, there is also ternary co-doping for non-metallic element doping of titanium dioxide nanoparticles, and among the ternary Co-doped elements, nitrogen has the best compatibility [6]. The precursor of this nitrogen element is urea. When the ratio of nitrogen element to titanium dioxide nanoparticles is one to one, the nitrogen element doped titanium dioxide nanoparticles alone have the best photocatalytic performance. Therefore, for the ternary co-doping of non-metallic elements, nitrogen and other non-metallic element (sulfur, fluorine, carbon, etc.) are often used as co-doping. Experiments have proved that for the co-doping of nitrogen and fluorine, titanium dioxide nanoparticles can obtain the highest photocatalytic activity [6].

Table 1. The influence of different dopants on the band gap of titanium dioxide [6,8-9]

Proportions of each element	Decomposed pollutants	Band gap
TiO ₂	/	3.26 eV
n (Fe ³⁺): n (nTiO ₂) =0.2%	azo dye methyl orange	3.17 eV
n (Fe ³⁺): n (nCu ²⁺): n (n TiO ₂) = 2.5%:7.5%:1	Methylene blue	2.75 eV
C/ TiO ₂	Methylene blue	2.37 eV
N/ TiO ₂	azo dye methyl orange	2.4 eV

4. Comparison of the Degradation Properties of Titanium Dioxide Nanoparticles in the Presence of Organic Matter

The method of using organic matter to degrade nano titanium dioxide from organic waste is relatively complex and is mainly divided into 2 types, the first is to synthesize greener and more efficient titanium dioxide using biosynthesis methods [10]. The second is to improve the photocatalytic activity of titanium dioxide nanoparticles by constructing metal-organic frameworks and combining organic ligands with inorganic materials [11].

The biosynthetic method is an economical, efficient, and environmentally friendly way to synthesize the required substances. The main biological precursors required for the synthesis method are mainly microorganisms, enzymes, and plant extracts [12]. Among them, plant extracts are the most suitable biological precursors in terms of economic cost, environmental protection, and oxidation-reduction characteristics [10]. Sahar et al. used different plant extracts as biological precursors to prepare titanium dioxide nanoparticles with better performance, using methyl orange as organic waste to test the differences in photocatalytic degradation of titanium dioxide nanoparticles prepared from different plant extracts. The final test results showed that under certain conditions, titanium dioxide nanoparticles prepared from plant extracts have better photocatalytic properties, while other variables remain the same [10]. Metal-organic framework is a combination of organic and inorganic. For example, amino groups are used as organic ligands to cooperate with other inorganic components such as titanium dioxide to finally obtain a new type of metal-organic framework, which greatly improves photocatalytic efficiency [13].

5. Conclusion

Overall, titanium dioxide nanoparticles, as an excellent semiconductor, exhibit remarkable optical properties. However, they face challenges such as a wide band gap and a high electron-hole recombination rate. To address these issues, previous researchers have proposed compositing inorganic metals or non-metals with titanium dioxide nanoparticles to narrow the band gap and enhance photocatalytic degradation performance. Among inorganic metals, trivalent iron is predominantly used for doping; however, studies attempting co-doping with multiple inorganic metal elements have shown limited success, often resulting in reduced photocatalytic performance. Among

inorganic non-metals, carbon and nitrogen are the primary dopants, with nitrogen being the most extensively utilized. The morphology and structure of titanium dioxide play a crucial role in its performance. For instance, some researchers have achieved excellent photocatalytic performance by synthesizing titanium dioxide nanotubes via the hydrothermal method and compositing them with urea. Therefore, when considering the compositing of different materials with titanium dioxide nanoparticles, the preparation methods ensuring proper morphology and purity of titanium dioxide nanoparticles are critical. Co-doping titanium dioxide nanoparticles with both inorganic metals and non-metals may offer potential improvements in photocatalytic performance. In addition, green synthesis of titanium dioxide nanoparticles, or the construction of a metal organic framework with organic ligands and Co doped composite inorganic semiconductors, will also be a way to improve the photocatalytic efficiency of titanium dioxide nanoparticles.

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