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Photocatalytic Degradation of Organic Pollutants in Wastewater by Tio_2

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ABSTRACT. *In this paper, the current research status of photocatalyst TiO_2 is summarized. The applications of TiO_2 photocatalytic degradation regarding the influencing factors, the reaction mechanism and the reaction of the active material are described in the paper. The TiO_2 modification methods (physical modification, chemical modification such as doped with single element and multiple elements, and two-component modifying) used in the photocatalytic reaction are detailed in this paper. By summarizing the relevant research results of TiO_2 in the field of photocatalysis, it will help to improve the catalytic degradation capacity of TiO_2 in the future and make greater progress in the field of environmental science.*

KEYWORDS: *Tio2 photocatalytic degradation, Reaction mechanism, Physical modification, Chemical modification*

1. Introduction

With the rapid development of modern society, the density of production and living has increased, and the problem of water pollution has become increasingly serious [1]. The main sources of water pollution in modern life include industrial production wastewater, excessive use of pesticides [2], Azo dyes[3], and the use of a series of antibiotics and drugs [4].

Therefore, how to effectively degrade organic pollutants has been widely concerned, among which photocatalytic degradation of organic pollutants has been widely studied. A photocatalyst, TiO_2 is an ideal photocatalytic material due to its excellent optical properties and stability, low production cost and abundant raw materials. However, TiO_2 still has some limitations [5]. In this paper, the current research status of TiO_2 photocatalytic in degradation of organic matter is introduced, as well as different modification methods to improve its efficiency.

2. The Introduction of Tio_2

2.1 Crystal Structure and Preparation of Tio_2

In nature, TiO_2 has three crystal types, namely anatase type, rutile type and

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platinite type. Among them, photocatalytic TiO_2 commonly used has two crystal structures: anatase type and rutile type. Anatase type TiO_2 (3.2eV) has more surface active centers, so its photocatalytic activity is higher. In terms of thermal stability, rutile type tends to be stable. Rutile crystals are elongated and prismatic, usually twin crystals, anatase crystals are generally approximately regular octahedrons. Their spatial structure is shown in the following figure:

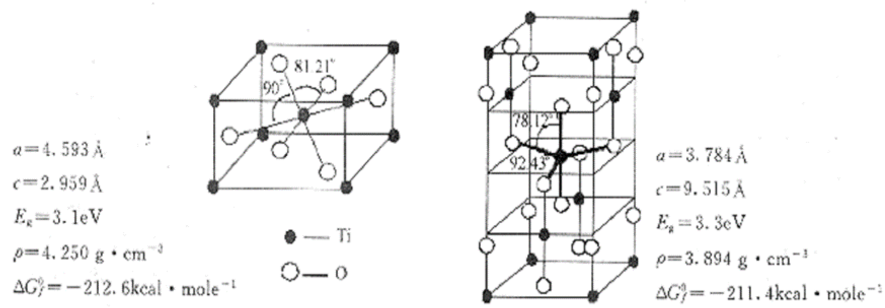

Fig.1 Crystal Structure of Tio_2

2.2 Photocatalytic Reaction Mechanism and the Reaction Process of Tio_2

2.2.1 Reaction Mechanism

When studying the mechanism of TiO_2 degradation of organic pollutants, people reached a certain consensus on the photocatalytic reaction mechanism of TiO_2. TiO_2 is an n-type semiconductor with a large energy difference between valence band and conduction band, making it a wide band gap semiconductor. When using higher than that of the conduction band and valence band energy difference of TiO_2 light irradiation, the valence band of TiO_2 electron stimulated transition to the conduction band, at the same time in the price causes cavitation on the belt, and make use of TiO_2 electronic - hole of oxidation reduction effect, toxic and harmful organic compounds can be finally oxidized to carbon dioxide and water and other inorganic small molecules, so as to achieve the effect of photocatalytic degradation of pollutants.

The process diagram of photocatalytic degradation of TiO_2 is as follows:

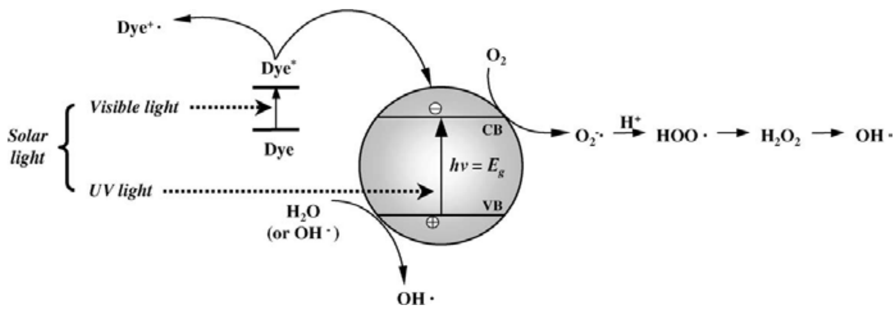

Fig.2 Photocatalytic Degradation of Tio2 [6]

2.2.2 Reaction Process and Intermediates

People studying the process of TiO_2 light degradation of organic pollutants found that in the degradation process, the TiO_2 photocatalyst plays as an electron carrier, facilitating the reaction between organic pollutants and TiO_2. Maria studied the photocatalytic degradation process and intermediate products of acidic orange 7 aqueous solution in TiO_2 suspension by using solar simulated light source [7]. The study found that the dye adsorbs on TiO_2, after a series of oxidation processes, makes it decolorize and generates many intermediates, mainly aromatic and aliphatic acids. These molecules are further oxidized to progressively lower molecular weight compounds and eventually to carbon dioxide and inorganic ions such as sulfate, nitrate, and ammonium.

3. Doping Study about Tio_2

In order to improve the efficiency of photocatalyst TiO_2 and the utilization ratio of materials, there have been many reports on TiO_2 doping. The quantum efficiency of photocatalysis can be improved to some extent by adding photosensitizer, introducing metal ions, transition metal ions, non-metal elements and other composite semiconductors. The recovery of TiO2 nanoparticles can be effectively solved by constructing semiconductor - insulator composite structure.

3.1 Composite Semiconductor Structure

Photoactive compounds (photosensitizers) are chemically or physically bonded to the surface of the photocatalyst. When exposed to the light, the photosensitizer excites electrons into the conduction band of the semiconductor, and the effect is the same as that of a single semiconductor.

Since photosensitizers can be excited by a wider wavelength range of light, the introduction of photosensitizers can improve the response of optical semiconductors to visible light. Guo Mei prepared TiO_2/ PG-C3N4 composite material [8] and

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conducted a certain study on it. The results show that the improvement of photocatalytic performance of TiO_2/ PG-C3N4 (5:100) is due to the increase of active sites of photocatalytic reaction in the porous structure. Besides, z-type heterojunction was formed between TiO_2 and PG-C3N4.

3.2 Noble Metal Deposition

When some precious metals (such as Pt and Au) are deposited on the surface of TiO_2, the recombination of electrons and holes can be inhibited. Fu Xianzhi [9] showed that platinum modified TiO_2 had higher degradation rate and mineralization rate for benzene than single TiO_2. Harade studied the degradation of organophosphorus pesticides in water by Pt/TiO_2 and found that the reaction rate was 6 times higher than that of TiO_2 [10].

3.3 Metal Element Doping

For metal element doping, take zinc element and platinum element doped TiO2 as an example, these elements can reduce the probability of capture of the electrons in conduction band, and improve electron transport rate, thus enhance reaction activity. Wang Zhenxing prepared nano-composite TiO_2-ZnO mesoporous composites and found that it could improve the photocatalytic activity and mineralization rate [11]. Using nanotube titanate as precursor, Jing Mingjun prepared platinum doped TiO_2 samples by low-temperature hydrothermal method. The results show that in the process of doping Pt metal, a large number of bound single-electron oxygen vacancies are generated, which improves the catalyst's ability to absorb visible light [12].

3.4 Doping of Transition Metal Particles

Appropriate transition metal ion doping can introduce lattice defects in semiconductor crystals to form more photocatalytic active sites, but too much doping will increase the number of carrier complex centers on the catalyst surface and reduce the activity. Choi studied the doping effect of 21 metal ions on TiO_2 and found that plasma doping 0.1% and 0.5% Fe^{3+}, Mo^{2+}, Ru^{2+}, Os^{2+}, Re^{5+}, V^{4+} and Rh^{3+} could improve the photocatalytic reaction activity of TiO_2, while Co^{2+} and Al^{3+} had negative effects [13].

3.5 Non-Metallic Ion Doping

Nonmetallic ion doping has been widely studied as an effective method to improve the photocatalytic activity of nano TiO_2. The non-metallic doping can not only reduce the band gap of nanometer TiO2, widen the response range of visible

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light, but also effectively inhibit the photogenic carrier compound rate, so as to improve its photocatalytic performance.

Deng Wei prepared amorphous sulfur doped TiO2 (S-TiO_2). The interaction between the amorphous type of S-TiO_2 catalyst and the Ti-O-S structure formed by S doping reduces the forbidden band of the catalyst and the absorption band is significantly redshifted, which enhances its photocatalytic activity under visible light.[14]. The N-TiO_2 prepared by Zhao Wenxia in the atmosphere of air and nitrogen calcined were all successfully mixed with N elements and were all anatase type. N-TiO_2 (N_2) has smaller grain size, larger specific surface area, stronger visible light response and higher effective nitrogen content than N-TiO_2 (air) [15].

3.6 Doping of Two Elements

At present, the research on double - element doped TiO_2 in China has made some progress and achieved some results. Because TiO_2 has fewer active sites and higher electron hole compound rate, the deficiency of TiO_2 can be greatly improved by doping two kinds of elements. Taking Zhu Baolin's study as an example, after the preparation of nitrogen-fluorine double-doped titanium nanotubes (N, F/TiO_2), the study found that the activity of TiO_2 nanotubes in simulated sunlight was significantly enhanced after the nitrogen-fluorine doping [16].

4. Physical Modification of Tio_2

The specific surface area of TiO_2 can be increased by means of physical modification (combined with glass or plastic tube, etc.) to expand the application of TiO_2. Chen Xinfu prepared TiO_2/SBA-15 composite material by post-synthesis hydrolysis method and different calcination temperature regulation using cheap and widely available ilmenite as raw material and highly ordered mesoporous structure as carrier. The results shows when the calcination temperature is 550 ℃, the specific surface area of TiO_2/SBA-15 is up to 386 m^2/g, and greatly increases the specific surface of TiO2. The degradation rate of methyl orange within 3 h was 85.1% and solution mineralization rate was 62.9%. TiO_2/SBA-15 composite material effectively improves the photocatalytic activity and maintained good stability, and improves the photocatalytic efficiency of TiO2 [17].

5. Photocatalytic Degradation of Tio_2 with Additional Substances

In the process of photodegradation, other substances can be added to improve the photodegradation performance of TiO_2, so as to expand the application of TiO_2. At present, there have been some studies on the photodegradation of TiO_2 involving external substances in China. Adding other oxides (H_2O_2, KIO_4, K_2FeO_4, etc.) as electron acceptors can produce synergistic effect with TiO_2, effectively inhibiting the reorganization of e^- and h^+.

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5.1 Adding H_2o_2 and Kio_4

Yu Zhiyong studied photodegradation catalyst TiO_2 or oxidant (H_2O_2, KIO_4) or its combination (TiO_2+ H_2O_2,TiO_2+ KIO_4) under ultraviolet illumination to degrade simulated water organic pollutant methyl orange [18]. The results showed that the photochromism of methyl orange was TiO_2+ KIO_4 >> KIO_4 > TiO_2+ H_2O_2> TiO_2 > H_2O_2, greatly increased the photodegradation efficiency of methyl orange.

5.2 Adding K_2feo_4

Zhu Liting used ferrate - photocatalysis synergistic process to degrade DMP in water in view of the refractory property of dimethyl phthalate (DMP). The effects of different parameters on the degradation efficiency of DMP were studied by adding certain TiO_2 photocatalyst and appropriate DMP to ferrate solution to simulate organic pollutant samples. The results show that the Fe (Ⅵ) - TiO_2 - UV system of DMP degradation rate is superior to other two kinds of systems (ferrate system and TiO_2 - UV degradation system), shows that the combination of photocatalytic and ferrate produce obvious synergistic effect[19].

6. Conclusion

This paper introduces in detail some modification methods for TiO_2, including physical modification and chemical modification such as element doping modification, to raise its range of light absorption and decrease the electron-hole recombination rate, which can further enhance the photocatalytic efficiency, etc.. The photocatalytic degradation of TiO_2 with some added substances is also introduced. The degradation rate of organic pollutants can be greatly improved by the synergistic action of the added substances and TiO_2. The spatial structure and reaction mechanism of TiO_2, other factors affecting the degradation of TiO2 are also described. With the help of the existing research results, including different modifications of TiO_2, the degradation ability of TiO_2 can be greatly improved, and the application of TiO_2 photocatalyst can be further expanded, so as to truly alleviate and even solve the problem of water pollution in the future.

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