Research progress of TiO$_2$-based photocatalytic materials

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Abstract. TiO$_2$ is the most widely studied photocatalyst, which has a good application prospect in the field of environmental pollution control and has always been a hot spot of photocatalytic materials research. The crystalline structure, surface morphology, and optical properties of TiO$_2$-based photocatalytic materials prepared by different methods are different, and thus exhibit different photocatalytic properties. In this paper, the research progress of TiO$_2$-based photocatalytic materials in China and abroad in recent years was reviewed based on the common preparation methods.

1. Introduction

The pollution problem caused by the rapid development of the industry is increasingly serious. The efficient and environmental degradation of various pollutants is an important issue related to the healthy development of the national economy. With the deepening of research, the use of photocatalytic materials to degrade harmful substances has shown a wide range of application prospects in the field of environmental protection, which is a green and sustainable technology [1-3]. Commonly used photocatalytic materials include ZnO [4], SnO$_2$[5], CeO$_2$[6], CdS [7], Ag$_3$PO$_4$[8], etc. Although there are many candidate materials for photocatalysis, TiO$_2$ has always been the core of photocatalytic materials research due to its high photocatalytic activity, non-toxic, low price, and stable chemical properties. It is also the most promising photocatalytic reference material for large-scale applications in the environmental protection and energy field [9-12]. The energy band structure of TiO$_2$ includes the valence band, conduction band, and the forbidden band between them. When excited by photons with energy greater than the forbidden bandwidth, the electrons in the valence band can transition to the conduction band, forming photogenerated electrons and leaving photogenerated holes in the valence band. The photogenerated electrons and holes migrate to the surface of the particles and react with the hydroxyl, water, and oxygen molecules adsorbed on the surface to generate hydroxyl radicals and superoxide radicals with strong oxidizing ability, which can directly oxidize organic pollutants to inorganic molecules such as carbon dioxide and water molecules to achieve the purpose of pollution control [13-15].

The photocatalytic activity of TiO$_2$-based photocatalytic materials is closely related to its preparation methods. The crystal structure, surface morphology, optical properties, and catalytic activity performance of TiO$_2$-based photocatalytic materials obtained by different preparation methods are different. According to different preparation methods, this paper summarizes the latest developments of TiO$_2$ photocatalysts in recent years and looks forward to the future research directions of TiO$_2$. 
2. Research progress of TiO$_2$-based photocatalytic materials prepared by sol-gel method

The Sol-gel method is one of the most commonly used methods for preparing nano-TiO$_2$ powder due to its simple process, small particle size distribution, and high purity[12, 16-20].

Sun Yue et al. [16] prepared pure TiO$_2$ powder by using butyl titinate as titanium source, glacial acetic acid as an inhibitor, and absolute ethanol as solvent under the condition of heat treatment at 500°C for 4h. Methylene blue (MB) was used as the target pollutant, and the effects of various process conditions on the photocatalytic performance of TiO$_2$ were investigated. The results showed that the photocatalytic performance of TiO$_2$ was the best when absolute ethanol, water, and glacial acetic acid were 28mL, 2.5mL, and 2mL, respectively. When 0.5g of prepared TiO$_2$ powder was added to 100 mL MB, the degradation rate was as high as 98.7% after 2 hours. But due to the shortcomings of insufficient solar utilization and the low quantum efficiency of pure TiO$_2$, it is necessary to modify it. The sol-gel method is simple and convenient to modify, and the modification effect is good.

Lan [17] et al. added lanthanum nitrate and boric acid during the process of preparing TiO$_2$ by the sol-gel method and obtained La and B co-doped TiO$_2$ photocatalyst after aging at 60°C for 16h and heat treatment at 400°C for 3h. The X-ray diffraction (XRD) results showed that the prepared TiO$_2$-based photocatalytic materials were all anatase structures, the grain size decreased after doping and the specific surface area increased from 57.07m$^2$/g of pure TiO$_2$ to 94.66m$^2$/g. The UV-Vis diffuse reflectance spectrum (DRS) showed that the forbidden bandwidth decreased after doping, which was beneficial to increase the utilization of visible light sources. The fluorescence spectrum (PL) showed that doping could improve the quantum efficiency by inhibiting the recombination of photogenerated electrons and holes. The photocatalytic experiment under visible light source showed that when the molar ratio of La/Ti is 0.5%, the activity of La-TiO$_2$ was the highest. After adding 3% B in molar ratio, 1%La-3%B-TiO$_2$ sample had the best photocatalytic performance. They believed that La and B co-doping had a synergistic effect on improving the photocatalytic activity of TiO$_2$. Because B doping could make the valence band move up, while La doping introduced the impurity level in the forbidden band, which was conducive to improving the photocatalytic performance.

The sol-gel method could also be associated with other methods used to construct TiO$_2$-based composite materials, such as JiaoYuRong[12] first prepared pure TiO$_2$ by the sol-gel method, and then synthesized the Ni-doped TiO$_2$/RGO composite photocatalytic material by the hydrothermal method. The scanning electron microscopy (SEM) showed that pure TiO$_2$ was spherical particles. After compositing with flake-like RGO, the Ni-doped TiO$_2$/RGO sample appeared porous morphology. TiO$_2$ was loaded on the surface of RGO, which improved agglomeration. The Photocatalytic experiment showed that the first-order reaction rate constant increased from 0.0093s$^{-1}$ for pure TiO$_2$ to 0.0124s$^{-1}$ for TiO$_2$/RGO and then increased to 0.0163s$^{-1}$ for Ni@TiO$_2$/RGO. The Ni@TiO$_2$/RGO prepared by this method had good recycling performance, and its degradation rate was still above 80% after 8 times of repeated use.

The combination of the sol-gel method and the dip-coating method is a common process for preparing TiO$_2$ thin films. Bensouici et al. [20] first prepared the TiO$_2$ sol by the sol-gel method. Then the glass substrate was placed in the sol, and then immersed and pulled to obtain a pure TiO$_2$ film. Then the TiO$_2$ film was modified by Cu doping to obtain a Cu doped TiO$_2$ film. The surface of the film was composed of TiO$_2$ particles, and the thickness of the film increased with the increase of Cu doping amount. The MB degradation experiment of the prepared film showed that the degradation rate of the pure TiO$_2$ film was the highest, but the degradation rate decreased after Cu doping, and the higher the doping concentration, the lower the degradation rate. They believed that Cu doping may introduce CuO and Cu$_2$O into the TiO$_2$-based materials, which was unfavorable to the separation of photogenerated electrons and holes, so the photocatalytic performance was lower than that of pure TiO$_2$ films.
3. Research Progress of TiO2-based Photocatalytic Materials Prepared by Hydrothermal Method

The hydrothermal method is conducive to the control of the morphology of the product and can change the hydrothermal process to construct TiO2-based photocatalytic materials with special morphologies such as granular [9, 21, 22], flower-like [23], and microsphere-like [24, 25].

Using butyl titanate and absolute ethanol as raw materials, Qin Bo et al [9] prepared pure TiO2 and Na2CO3 modified TiO2 at a certain hydrothermal temperature. The samples were all anatase structures, and the SEM photos showed that the products were grainy, with some agglomerations. After Na2CO3 modification, some porous structures appeared on the surface of the samples. The specific surface area increased from 55.00m2/g of pure TiO2 to 77.55m2/g, which increased the contact area between the photocatalyst and the reaction pollutants and was beneficial to the photodegradation process. The degradation experiment of MB showed that the degradation rate had increased from 70% of pure TiO2 to over 97%.

Duan et al. [22] prepared C-doped anatase/brookite mix-phase TiO2 by hydrothermal method and studied the influence of different C sources on the structure and photocatalytic performance of mix-phase TiO2. The results showed that when the C source was phenylene trihydroxybenzene, resorcinol, glycine, and ethylene glycol, the content of anatase gradually decreased and the content of brookite increased. The DRS and PL spectra confirmed that the introduction of C was beneficial to reduce the forbidden band width of TiO2 and inhibit the recombination of photogenerated electrons and holes. The photocatalytic experiment on rhodamine B (RhB) showed that when the C source was ethylene glycol, the photocatalyst activity was the highest, which was due to the lowest forbidden band width, the highest utilization rate of the light source and the best inhibition effect on carrier recombination.

Pawar et al. [23] used titanium tetrachloride as the titanium source and prepared TiO2 films on FTO glass by the hydrothermal process at 160℃ and 12h. They kept the content of water and hydrochloric acid constant during the preparation process and studied the effect of different amounts of titanium tetrachloride on the surface particle morphology of the film. The SEM images showed that when the amount of titanium tetrachloride was 0.4mL, the particles on the surface of the film were nanorods; when the dosage was 0.6mL, the particles on the surface of the film were flower-like composed of nanorods; when the dosage was 0.8mL, the particles were not only flower-like but also spherical; when the dosage was 1mL, the spherical morphology further increased and the flower-like morphology decreased.

Shen Minghu et al. [24] did not add a template in the process of preparing TiO2 and obtained TiO2 hollow microspheres by a one-step hydrothermal method. They studied in detail the effects of hydrothermal temperature and hydrothermal time on the morphology and photocatalytic activity of the microspheres. The XRD showed that when the hydrothermal temperature was 120 ℃ and 140 ℃, the samples were all anatase structure, and the crystallinity was good, indicating that the hydrothermal temperature had little effect on the crystal structure of the microspheres. In addition, they fixed the hydrothermal temperature at 140 ℃ and changed the hydrothermal time to obtain different samples. The SEM results showed that when the hydrothermal time was 2h, the diameter of the microspheres was about 1.8μm, and the particle size was about 40 nm, there was no obvious hollow structure. With the increase of hydrothermal time to 10h, TiO2 hollow microspheres with core-shell structures were formed. But when the hydrothermal time was further increased to 20h, the microspheres collapsed and broke. The BET results showed that the specific surface area of the prepared microspheres was 70m2/g, significantly higher than that of commercial P25 (50m2/g). In addition, the photocatalytic experiment results showed that the photocatalytic activity was the highest when the hydrothermal temperature was 140℃. Under the condition of a fixed hydrothermal temperature of 140℃ and a hydrothermal time of 14h, the photocatalytic performance was the best.
4. Research progress of TiO2-based photocatalytic materials prepared by anodic oxidation

The anodic oxidation method can be used to prepare highly ordered TiO2 nanotube arrays. The TiO2 nanotubes prepared by this method have high specific surface area, unique electron transport path, and high quantum efficiency, which have attracted much attention in recent years [26-30].

Cheng Xianxiong et al. [26] first polished the titanium plate, cleaned it by ultrasound, then added ethylene glycol, ammonium fluoride, and other raw materials to prepare electrolyte, and finally controlled the electrolysis parameters to generate TiO2 nanotubes on the titanium plate by anodic oxidation method. The SEM images showed that the inner diameter of the nanotubes was uniform, and the diameter of the nanotubes was between 30nm and 45nm. The crystal structure of the nanotubes was a mix-phase structure of anatase and rutile. In addition, they also studied the influence of electrolysis parameters on the photocatalytic activity. The degradation experiment of cefotaxime sodium showed that the degradation rate was the highest when the voltage was 30V, the time was 6h, the plate distance was 5cm, and the mass fraction of ammonium fluoride was 0.3%.

The photocatalytic performance can be further improved by doping modification when prepared by anodic oxidation. Li et al. [29] first prepared pure TiO2 nanotubes and studied the effects of reaction time and electrolysis voltage on their crystal structure. The results showed that extending the reaction time and increasing the electrolysis voltage was beneficial to the crystal integrity of anatase TiO2 and the increase in crystallinity. On this basis, Gd was introduced during the preparation of TiO2 nanotubes to obtain Gd-doped TiO2 nanotubes with a specific surface area of 176 m2/g. In fact, the crystal structure of the nanotubes was not changed by Gd doping, and the nanotubes were still anatase. The SEM images displayed that the length of Gd-doped TiO2 nanotubes was about 50μm and the tube diameter was about 100nm. Compared with pure TiO2 nanotubes, the morphology of Gd-doped TiO2 nanotubes had no significant change. In addition, the photodegradation experiment of methyl orange (MO) showed that the pure TiO2 nanotubes had the highest activity when the reaction time was 10h and the electrolytic voltage was 60V, but the activity of Gd-doped TiO2 nanotubes was higher than that of pure TiO2. When the doping amount of Gd was 0.01mol, the activity of Gd-doped TiO2 nanotubes was the highest.

5. Research progress of TiO2-based photocatalytic materials prepared by other methods

In addition to the above three methods, the preparation methods of TiO2-based photocatalytic materials include ion exchange method [31, 32], precipitation method [33, 34], microemulsion method [35], and other synthetic processes.

Wang et al. [31] prepared TiO2 whiskers using potassium titanate as raw material by the ion-exchange method, and then the whiskers were calcined at 700°C, anatase TiO2 appeared. However, when the temperature was 950°C, a mix-phase structure of anatase and rutile appeared, and when the temperature was 1100°C, it was completely transformed into rutile TiO2. The prepared TiO2 whiskers were 5-15μm in length and 100-200nm in diameter. The photocatalytic experiment results showed that the sample had the highest activity after calcination at 700°C.

Song et al. [33] used (NH4)2TiF6 and CO(NH2)2 as raw materials, and finally prepared flower-like porous TiO2 after heat treatment at 550°C for 2h by the homogeneous precipitation method. The XRD results showed that the sample was single anatase, and the crystallinity of the sample was improved after calcination, so it exhibited higher photocatalytic activity.

Gao Song et al. [35] used butyl titanate as raw material and polymer copolymer F127 as the template to synthesize mesoporous pore TiO2 in the microemulsion system of Span-20 and Triton X-100/cyclohexane/n-butanol/water. And then the samples were calcined at 350°C-450°C to obtain anatase TiO2. The results showed that the increase in temperature was conducive to the integrity of the crystal form and the improvement of crystallinity. On the other hand, the increase in temperature would reduce the specific surface area of mesoporous pore TiO2. In short, the photocatalytic activity of the mesoporous TiO2 prepared by adding the template agent was higher than that of the non-mesoporous TiO2. This was because the porous structure increased the specific surface area, which was beneficial to adsorb organic molecules.
6. Conclusion
As the most widely studied photocatalytic material, TiO$_2$ has broad application prospects in the field of environmental protection, and its photocatalytic performance is closely related to the preparation method. According to the above review, each method has its own advantages and disadvantages. Among the same method, the best preparation process and modification process are also different. Therefore, seeking the best process route to obtain cheap, simple and high catalytic activity TiO$_2$-based photocatalytic materials is still the focus of future research.

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