Construction of High Activity Titanium Dioxide Crystal Surface Heterostructures and Characterization of Its Basic Properties

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Abstract Heterogeneous photocatalytic materials, which combine the advantages of photocatalytic materials and heterojunction, have been developed rapidly in the field of environmental pollution control. In this paper, TiO₂ surface heterojunction catalysts with different catalytic activity were prepared by controlling the amount of HF, and their XRD characterization was also carried out. In addition, the optimum amount of HF was determined by photocatalytic degradation of simulated dye wastewater by methylene blue solution. And the optimal amount of catalyst and the optimal pH reaction conditions for degradation experiments were used to screen the highly reactive titania surface heterojunction system and its optimum application conditions. It provides the possibility of application in the degradation of industrial wastewater and environmental treatment.

1. Introduction
TiO₂ is a wide bandgap n-type semiconductor, with high energy absorption of ultraviolet light has a strong absorption capacity. When TiO₂ is irradiated with light, an electron-hole pair is formed [1], and OH⁻ and H₂O adsorbed on the surface of TiO₂ are oxidized to produce active substances such as hydroxyl radical (·OH) having strong oxidizing properties, and OH is added to the organic matter in water Mineralized into CO₂ and H₂O [2, 3]. TiO₂ is a non-toxic, stable performance of the new catalyst, it is no degradation of organic compounds in water, no secondary pollution. Nano-TiO₂ has a huge surface area, the greatest degree of degradation of organic matter in wastewater, widely used in industrial wastewater treatment and new energy development and utilization [4].

However, TiO₂ as a wide bandgap material, will only be short wavelength of ultraviolet light excitation, which is the use of ultraviolet light content of only 4% of the sun is extremely
unfavorable [5, 6]. In addition, the photo-generated electron-hole generated by the use of light is high, so that the photonic efficiency is low and the photocatalytic performance is not prominent [7, 8]. This is also the main reason for the limitation of the photocatalyst of the semiconductor type in the practical application. While the heterogeneous junction of the built-in electric field can inhibit the photo-charge charge, improve the quantum efficiency, if the TiO₂ and narrow-band semiconductors constitute heterojunction, narrow-band semiconductor sensitization can expand the response spectrum of TiO₂, promising to overcome the above-mentioned TiO₂ Disadvantages [9, 10].

The interfacial regions formed by the contact of two different semiconductors are heterojunction, and the photocatalytic properties of TiO₂ with different crystal phases are different, which is due to the different structure [11, 12]. Nano-heterojunction photocatalytic materials combine the advantages of nanomaterials and heterojunctions and are rapidly developing in the field of environmental pollution control [13, 14]. Zheng et al. Successfully synthesized the titanium dioxide crystals with the {001} ratio of 45%, 69% and 82% by hydrothermal method, and the yield of active hydroxyl groups (·OH) and the yield of H₂ were characterized by three Photocatalytic properties of materials. The results show that the higher the proportion of {001} crystal face, the lower the photocatalytic performance of the material [15, 16].

In this paper, we studied the preparation of TiO₂ surface heterojunction with different photocatalytic properties by controlling the addition of HF, and explored the influence factors of catalyst dosage and pH during the photocatalytic degradation of methylene blue solution, and screened the best TiO₂ crystal face Heterojunction system and its optimal reaction conditions.

2. Experimental

Titanic acid four butyl ester (C₁₆H₃₆O₄Ti, chemical purity, Sinopharm Chemical Reagent Co., Ltd.). Hydrofluoric acid (HF, analytical pure, Aladdin Industrial Corporation). Methylene blue (C₁₆H₁₈ClN₃S, 3H₂O, analysis of pure, Tianjin Municipality kemiou Chemical Reagent Co., Ltd.). Anhydrous ethanol (C₂H₅OH, analytical purity, Tianjin Fuyu Fine Chemical Co., Ltd.). The water used in the experiment was deionized water.

2.1 Preparation of Titanium Dioxide

2.5 ml, 3 ml, 3.5 ml and 4 ml hydrofluoric acid were added into the plastic beaker containing 25 ml titanic acid four butyl ester, and the beaker was placed on a magnetic stirrer to stir 30 min to make it dissolve evenly. Then, the solution in the beaker was transferred into the reaction kettle and reacted in 180°C for 24h to obtain white precipitate. The white precipitate was washed three times with anhydrous ethanol and deionized water. The impurities were removed, and then the TiO₂ precipitate was obtained. Four different titanium dioxide crystal powders were obtained by freeze drying of TiO₂.

2.2 Characterization

The samples structure was characterized by powder X-ray diffraction (XRD) using a scanning rate of 0.05 °/s within a 20 range of 10°–80° (Bruker D8 Advance; Cu Kα=1.5404 Å) [17].
2.3 Determination of photocatalytic activity
The photocatalytic activity was determined by absorbance changes of methylene blue solution (MB solution, 10 ppm) in a certain amount of photocatalytic reactor [18]. A 500 W xenon lamp with internal irradiation was used as light source. A 250 mL beaker was used as the reactor loading. The distance between the center of the light source and the beaker mouth is about 5 cm. Before the photocatalytic experiment, the mixed solution was stirred for 30 minutes in the absence of light so as to make the mixed solution reach the adsorption equilibrium. During the experiment, the magnetic stirrer at the bottom of the beaker continues to stir the reaction solution to ensure that the reaction solution and the catalyst are mixed evenly during the experiment. 0.125 g photocatalyst was added into 150 mL MB solution to form suspension and homogenized by ultrasonic vibration. 5 mL mixed solution was taken at intervals of 10 minutes and filtered by 0.45 µm microporous filter. Absorbance was measured at 664 nm by visible spectrophotometer.

3. Results and discussion

3.1 Characterization of the TiO2 Crystal Surface Heterostructures
The crystal shape and crystallinity of the prepared samples were further analyzed by XRD. As shown in Fig. 1, the XRD pattern of the prepared titanium dioxide heterojunction was obtained when the addition amount of hydrofluoric acid was 2.5 mL, 3 mL, 3.5 mL, 4 mL. It can be concluded from the figure, the diffraction peak of TiO2 at 25.3°, 38.1°, 48°, 53.9°, 54.8°, 62.8°, 69.4°, 70.5° and 75.1° respectively corresponding to the crystal phase (101), (004), (200), (105), (211), (204), (116), (220) and (215) crystal [19]. All the peaks are in accordance with the standard card (JCPDS card number: 73-1764). Four kinds of TiO2 crystalline surface heterostructures are pure anatase phase of TiO2. The Miscellaneous peak of TiO2 crystal heterojunction with HF addition of 3.5 mL and 4 mL is caused by excessive concentration of F-. 

![Figure 1. XRD Characterization of Titanium Dioxide under Different Preparation Conditions. 4 mL: Hydrofluoric acid was added in an amount of 4 mL; 3 mL: Hydrofluoric acid was added in an amount of 3 mL; 3.5 mL: Hydrofluoric acid was added in an amount of 3.5 mL; 2.5 mL: Hydrofluoric acid was added in an amount of 2.5 mL;](image)
Normally, the crystal structure of anatase TiO$_2$ is a cross section eight body double cone, which includes eight \{101\} surfaces on the side and two \{001\} surfaces at the top and bottom. Research shows that with the increase of HF content, the intensity of XRD peak and XRD peak samples is more stable, the width is more and more narrow, indicating that TiO$_2$ crystallinity increases, the percentage of \{001\} is more and more high that F- plays a key role in the formation of TiO$_2$ Nano plate. [20]. The \{001\} percentage of the corresponding amount of HF is shown in Table 1.

**Table 1.** Physicochemical Properties of Different Samples

| sample | HF(mL) | \{001\} facets\% |
|--------|--------|-----------------|
| HF2.5  | 2.5    | 46              |
| HF3    | 3      | 49              |
| HF3.5  | 3.5    | 52              |
| HF4    | 4      | 55              |

3.2 Photocatalytic activity

The photocatalytic activity of the catalyst was determined by the degradation of methylene blue solution.

Figure. 2(a). Results of photocatalytic degradation of methylene blue solution, by TiO$_2$ crystal surface heterojunction prepared with different HF addition. It can be seen from the diagram that when the amount of HF increases gradually from 0-3 mL, the photocatalytic activity also increases; When the amount of HF is more than 3 mL, with the increase of HF, the photocatalytic activity decreases gradually, This is because the appropriate ratio of the \{001\} and the \{101\} surface can significantly reduce the recombination rate of the photoinduced electron and hole. However, the HF value greater than 3 leads to a higher percentage of \{001\} surface, which makes recombination recombination of electron holes. Therefore, the best amount of HF added to the photocatalytic activity of TiO$_2$ crystal surface heterojunction is 3mL.

Figure.2(a) Photocatalytic Performance of different TiO$_2$ catalysts; (b) catalytic effect diagram of different dosages of catalyst; (c) Influence Diagrams of different pH on catalytic performance of catalysts

Figure. 2(b) is the result of the influence of the dosage of TiO$_2$ catalyst on the photocatalytic performance. According to the diagram, the degradation effect of methylene blue solution is not significant when the dosage of catalyst is 0.0625 g. In addition, when 0.25 g catalyst was used to degrade methylene blue solution, the whole degradation process was
almost completed in the adsorption stage of the first 30 min. Therefore, the experimental results have no reference value. When the dosage of catalyst is 0.125 g, the concentration of methylene blue solution decreases gradually with the increase of time, and the effect is outstanding, so 0.125 g is the best catalyst dosage.

Figure 2(c) is a comparison of photocatalytic performance of TiO2 catalyst under different pH conditions. It can be seen from the diagram that when the methylene blue solution pH=2 gradually increases to pH=6, the photocatalytic activity also increases. When the pH value is greater than 6, the photocatalytic activity decreases with the increase of pH value. Therefore, the optimum pH value of TiO2 catalyst for methylene blue solution degradation was 6.

4. Conclusions
In this paper, TiO2 crystal surface heterojunction catalyst with different catalytic activity was prepared by controlling the amount of HF. The optimum amount of HF was determined by photocatalytic degradation of methylene blue solution. And the optimal dosage of catalyst and the optimal pH reaction conditions for degradation experiments. The final results are as follows:
(1) When the amount of HF is 3 mL, the photocatalytic performance of the TiO2 crystal surface heterojunction catalyst is the best.
(2) The optimum dosage of catalyst for photocatalytic degradation of methylene blue solution was 1.25 g.
(3) Optimum pH=6 for photocatalytic degradation of methylene blue solution.

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