Preparation and Photocatalytic Activity of TiO₂ Film with High Exposure {001} Crystalline Surface

Chunhua Yuan and Huimin Yang

College of Chemistry and Chemical Engineering, Inner Mongolia University of Science & Technology, Baotou 014010 China
Email: yuanchunhua79@126.com

Abstract. TiO₂ films with exposed {001} crystal surface were prepared by hydrothermal method with 10 mm * 20 mm * 0.15 mm titanium sheet as titanium source and substrate and HF as shape control agent. The films were characterized by (XRD), (SEM) and (UV-VIS). The results showed that the TiO₂ films with high exposure {001} crystal surface could be obtained by using 0.01 mol/L HF, 11:5 mixture of water and isopropanol as solvent, hydrothermal reaction temperature of 180°C, reaction time of 3H and calcination at 450°C for 2h. In this paper, methylene blue was used as probe and xenon lamp was used as light source to study the photocatalytic activity of TiO₂ film.

1. Introduction

In recent years, the controllable synthesis of inorganic nanoparticles with high active surface has attracted widespread attention, mainly because of their excellent performance in catalysis, photoelectric transformation and so on. Due to the special arrangement of surface atoms, the highly active exposed surface has more redox sites, which greatly improves the catalytic activity of nanoparticles[1]. However, due to the principle of minimum surface energy, the high active surface will gradually disappear in the process of crystal growth. Therefore, the efficient and controllable synthesis of inorganic nanoparticles with high active surface has become one of the hot spots in nano science and technology research[2].

TiO₂ has the advantages of moderate band gap energy, strong adsorption capacity for pollutants and high photocatalytic activity[3], and it is non-toxic, stable and cheap. It has the functions of self-cleaning, deodorization and sterilization. So it has become one of the most valuable catalysts in the field of environmental pollution control. There are two main problems in the practical application of TiO₂ as a photocatalysis material[4]: first, TiO₂ has a wide energy gap (3.0-3.2ev) and a narrow spectral response range, which leads to a low utilization rate of light (2-3%); second, TiO₂ has a high recombination rate of photogenerated electrons and holes and a low diffusion rate of thermal carriers[5], which leads to a low quantum efficiency as a photocatalysis material.

In this paper, TiO₂ films with exposed {001} crystal surface were prepared by hydrothermal method with titanium sheet(10 mm * 20 mm * 0.15 mm) as titanium source and substrate and HF as shape control agent. In the process of preparation, the controllable growth of micro crystal surface and the defect control of TiO₂ self-modification are used to greatly improve the catalytic efficiency and visible light utilization of TiO₂.
2. Materials and Methods

2.1. Materials
Instruments: electronic analytical balance (FA1004 Shanghai Hengping Scientific Instrument Co., Ltd.), digital display thermostatic water bath (HH-6 Shanghai Pudong physical optics instrument factory), electric thermostatic drying oven (101 Beijing ever-bright medical instrument factory), X ray diffraction (Rigaku-12KW Japan), tungsten (40W Lianhua Lighting Co., Ltd.) 722s visible spectrophotometer (Shanghai precision scientific instrument Co., Ltd.).

Reagent: Titanium plate(10 mm * 20 mm * 0.15 mm), oxalic acid, hydrofluoric acid, isopropanol, methylene blue, which was the analytical reagent.

2.2. Preparation of TiO$_2$ Film by Hydrothermal Method
First, titanium was put into 10% oxalic acid solution, and oxalic acid was heated to boiling. The titanium sheet was soaked in hot solution for 1h, then which was taken out and washed with deionized water for many times, and when was put into high-pressure reactor. The reaction conditions were as follows: the ratio of water and isopropanol was 11:5, appropriate amount of HF was added, hydrothermal reaction temperature was 180°C, reaction time was 180 mins. Then, the titanium sheet was taken out, washed and dried, then put into muffle furnace for baking with proper temperature and 120mins. Finally, TiO$_2$ films were obtained.

2.3. Characterization of Composite Materials TiO$_2$ Film
The matter phase is analyzed by D/Max-3cX of X-ray powder diffraction (XRD), and SEM, and UV-visible absorption spectrum etc.. The test conditions of XRD : Cu Target ka line, the Ni filter, the 40kV, 40mA, scanning range 20° ~ 80°(2θ), scanning speed 2°/min using X-ray diffraction.

2.4. Photocatalytic Properties of Composite Materials TiO$_2$ Film
Xenon lamp was used as a visible light source, and the light distance was 10 cm. The photocatalytic reaction process was: (1) a certain amount of TiO$_2$ film composite powder was added to methyl orange solution of 10mg/L; (2) firstly, in the absence of light, the solution was ultrasonic dispersed for 3min and magnetic stirred for 10 min, so that the organic molecular reached adsorption / desorption equilibrium on the catalyst surface; (3) with the light source opening, the photocatalytic reaction was carried out at room temperature, and the suspension system was kept magnetic stirring during the whole process of the photocatalytic reaction; (4) every 20 min beginning the light open, 5mL suspension sample was removed and centrifuged 10 min, then the upper liquid was absorbed, the solution absorbance of light catalytic was measured with 722S visible spectrophotometer in 665nm.

$$\eta = \frac{(A_0 - A_1)}{A_0} \times 100\%$$

Type: The $A_0$ and $A_1$ was respectively absorbance value of before and after the degradation of methylene blue solution at the maximum absorption wavelength.

3. Results and Discussion

3.1. XRD Analysis of Composite Catalyst TiO$_2$ Film
Fig.1 is the XRD detection of TiO$_2$ films prepared by hydrofluoric acid of different concentrations. It can be seen from Fig.1 that the main crystal form of the crystal is anatase with a small amount of rutile. In Fig. 1, the strongest absorption peaks of a and B lines appear at 2θ=25.576° and 2θ=37.692°. Theoretically, anatase type TiO$_2$ with {101} surface and {004} surface is25.3° and 37.8° respectively, because {004} surface is the fourth diffraction peak of {001} crystal surface, which indicates that the high exposure {001} crystal surface anatase type TiO$_2$ material has been prepared in the experiment[6]. The results show that HF concentration has an effect on the exposure of {001} crystal surface. By controlling HF concentration, anatase TiO$_2$ materials with different exposure degree of {001} crystal surface can be prepared.
In the experiment, XRD was used to analyze the crystal structure of the films prepared at different calcination temperature. It can be seen from Fig. 2 that the peak value of {004} in the curve C with the calcination temperature of 450°C is relatively prominent, which indicates that the exposed proportion of {001} crystal surface is relatively high. The peak values of {101} and {004} are almost the same in the curve B of calcination temperature of 400°C, and {004} is lower than {101} in the curve a of calcination temperature of 500°C. The reason is that the {001} surface will be reconstructed at 475°C in the anatase TiO$_2$, which results in the decrease of the exposed ratio of {001} surface.

Most of the peaks of curve B and C correspond to the anatase phase of titanium dioxide, and the high peak value of rutile in curve a indicates that its proportion is large. The results show that the anatase TiO$_2$ photocatalyst with high activity exposure {001} crystal surface can be prepared by controlling the calcination temperature to 450°C and HF concentration to 0.01 mol / L.

![Figure 1. XRD of TiO$_2$ films prepared with different HF concentration](image1)

![Figure 2. XRD of TiO$_2$ thin films prepared at different calcination temperatures](image2)

### 3.2. SEM Analysis of TiO$_2$ Film

In order to explore the influence of HF concentration on the surface morphology of TiO$_2$ films, the surface of TiO$_2$ films prepared with different HF concentration was examined by SEM, and Fig. 3 was obtained. A, B and C in Fig. 3 are TiO$_2$ films prepared when HF concentration is 0.01mol/L, 0.03mol/L, 0.05mol/L respectively. Figure 3d is the SEM comparison of pure Ti without hydrothermal reaction after pretreatment.

Figure 3a shows that TiO$_2$ products are all microsphere with regular spherical structure and good dispersion. In Fig. 3b, most of the TiO$_2$ microspheres are fused and connected together. Instead of being microspheres, they form strips along the irregular area, and a small number of polyhedral titanium dioxide particles are accumulated in the holes. Compared with figure a, the dispersion of TiO$_2$ particles in Figure B is poor. In Figure 3c, the fusion connection phenomenon is more serious, and the surface of Ti sheet is completely covered. On this layer, octahedral TiO$_2$ particles with smaller diameter and worse dispersion continue to grow.

The experimental results show that HF can be used as a shape control agent in hydrothermal reaction, which can be adsorbed on the {001} surface of TiO$_2$ to reduce its surface and make the crystal grow along the surface; with the increase of HF concentration in the experiment, the exposed proportion of TiO$_2$ high-energy crystal surface will increase. However, HF will corrode the surface of titanium dioxide, and the corroded TiO$_2$ microspheres are connected to form strips and thin layers. High concentration of HF is beneficial to the formation of high energy crystal surface of titanium dioxide, but with the increase of HF concentration, the aggregation and surface corrosion of TiO$_2$
microspheres will be intensified, and the photocatalytic activity of the film will be reduced, so the high concentration of HF will have a negative impact on the morphology of TiO$_2$. The experimental results show that when the HF concentration is 0.01mol/L, TiO$_2$ microspheres with high exposure {001} crystal surface can be obtained, and its dispersion is good, specific surface area is large, the film is less eroded, and its photocatalytic activity is better.

In order to further explore the influence of calcination temperature on the film forming, SEM tests were carried out on the film surface with calcination temperature of 400°C, 450°C and 500°C, and three pictures of a, B and C in Fig. 4 were obtained.

As shown in Fig. 4a, some areas of TiO$_2$ microspheres with different sizes and particle size distribution are connected together. In picture b of Fig. 3 & 4, the TiO$_2$ microspheres have regular structure, its particle size distribution is very centralized and its dispersion is good. In Fig. 4c, TiO$_2$ microspheres are enriched on the surface to form a thin layer. The surface of Ti sheet is completely covered by TiO$_2$ microspheres, and the diameter of the microspheres is smaller, but cracks appear on the surface of the material, which is due to the damage of the film caused by high temperature. The photocatalysis experiment also further proved that the catalytic materials with cracks are more likely to fall off and lose in the catalysis.

![Figure 3](image_url)

Figure 3. SEM of TiO$_2$ Prepared with different HF concentration

a(0.01mol/L)  b(0.03mol/L)  c(0.05mol/L)  d(Before experiment)
3.3. Study on Photocatalytic Properties of TiO$_2$ Film

Fig. 1 In this paper, the photocatalytic properties of TiO$_2$ film were studied. In the experiment, xenon lamp was used as the simulation light source, methylene blue was used as the target degradation material, and the effects of HF concentration and calcination temperature on the photocatalytic performance of TiO$_2$ film were studied respectively, as shown in Fig. 5 and Fig. 6.

a. Effect of HF concentration on Photocatalytic Performance of TiO$_2$ in pretreatment

Three lines of (a, b, c) in Fig. 5 are the curves of degradation rate of TiO$_2$ to methylene blue when HF concentration is 0.01mol/L, 0.03mol/L, 0.05mol/L respectively. line (d) in Fig. 5 is the degradation rate curve of methylene blue without photocatalyst.

It can be seen from Figure 5 that the catalyst prepared at the HF concentration of 0.01mol/L has the highest degradation rate and the best catalytic effect to methylene blue. The results of XRD and SEM analysis show that TiO$_2$ Prepared at this concentration has a highly exposed {001} crystal surface, its structure is regular spherical, and its dispersion is the best. This further proves that the TiO$_2$ with highly exposed {001} crystal surface has better photocatalytic effect.

b. Effect of calcination temperature on Photocatalytic Performance of TiO$_2$

Three lines of (a,b,c) in Figure 6 are respectively the degradation rate curve of methylene blue degraded by TiO$_2$ prepared at the calcination temperature of 450°C, 400°C, and 500°C. Line(d) in Fig. 5 is the degradation rate curve of methylene blue without photocatalyst.
It can be seen from Fig. 6 that curve a at 450 °C has the best catalytic degradation rate. It can be seen from Fig. 2 and Fig. 4 that when the calcination temperature is too low, it is not conducive to the growth of TiO\textsubscript{2} Crystal, but when the calcination temperature is too high, the photocatalytic effect of the calcined sample is relatively poor. This is because when the calcination temperature is too high, the amount of rutile phase in the crystal increases, and the exposure ratio of anatase phase {001} crystal surface also decreases. High temperature will also lead to the agglomeration of titanium dioxide and the reduction of specific surface area of catalyst. The degradation rate curve also confirms the conclusion in Fig. 2 and Fig. 4 that 450 °C is the best calcination temperature for preparing TiO\textsubscript{2}.

4. Conclusions
In this paper, TiO\textsubscript{2} film with exposed {001} crystal surface was prepared by hydrothermal method with Ti (10mm*20mm*0.15mm) sheet as titanium source and substrate and HF as shape control agent. The products were characterized by XRD and SEM. The results showed that TiO\textsubscript{2} film with high exposed {001} crystal surface was prepared. The photocatalytic activity of TiO\textsubscript{2} film was studied with methylene blue as probe. Under the irradiation of xenon lamp, the experimental conditions were controlled as HF concentration was 0.01 mol/L, the mixed liquid with ratio of water to isopropanol 11:5 was used as the hydrothermal reaction medium, the hydrothermal reaction temperature was 180°C, the reaction time was 180 mins, the calcination temperature was 450°C, the calcination time was 120 mins, then the product with the best catalytic performance was prepared.

5. Acknowledgement
This research was financially supported by the Natural Science Foundation of Inner Mongolia (No.2017MS(LH)0209 ), and National Natural Science Foundation of China(21902080)

6. References
[1] Maxwell Selase Akple, Jingxiang Low.Zhiyang Qin. Nitrogen-doped TiO\textsubscript{2} microsheets with enhanced visible light photocatalytic activity for CO\textsubscript{2} reduction[J], Chinese Journal of Catalysis, 2015, 36,(12):2127-2134.
[2] Qian Jianguo, Zou Yidong , Xue Xuan ect. Synthesis of Cu\textsubscript{2}O Single Crystals with Exposed {110} Facets and Its High Performance on Thermal Decomposition of Ammonium Perchlorate[J]. Journal of the Chinese Ceramic Society, 2016,44,(7):1040-1045.
[3] X. Y. Zhang, H. P. Li, X ,L. Cui, et al., Graphene/TiO\textsubscript{2} nanocomposites: synthesis, characterization and application in hydrogen evolution from water photocatalytic splitting, [J]. Mater. Chem., 2010,20: 2801-2806.
[4] N. Li, G. Liu, C. Zhen, et al., Battery performance and photocatalytic activity of mesoporous anatase TiO\textsubscript{2} nanospheres/graphene composites by template-free self-assembly, Adv. Funct. Mater., 2011,21:1717-1722.
[5] XU H, OUYANG S X, LI P, et al. High-active anatase TiO\textsubscript{2} nanosheets exposed with 95% {100} facets towards efficient H\textsubscript{2} evolution and CO\textsubscript{2} photoreduction [J]. ACS Appl Mater Interfaces, 2013, 5(4): 1348-1354.
[6] PAN J, LIU q LU Q, et al. On the true photoreactivity order of {001},{010}, and {101} facets of anatase TiO\textsubscript{2} crystals [J]. Angew Chem Int Ed, 2011, 50: 2133-2137.