Study on Photocatalytic Properties of TiO$_2$ with Special Morphology by Using Natural Template

Zhang Menglin$^{1,a,*}$, Guo Qingxin$^{1,b}$,

$^1$Xiamen University, Siming South Road 422, Siming District, Xiamen City, Fujian Province, 361005 China

$^a$ zhangmenglin1990@gmail.com, $^b$ steven_guoqingxin@gmail.com

*Corresponding Author

Abstract: The TiO$_2$ photocatalysts with special morphology were synthesized in this paper. The authors used malus micro malus leaves and in docalamus leaves as template, and tetrabutyl titanate (TBT) as Ti source. The special shaped TiO$_2$ photocatalysts have high photocatalytic activity because of its unique morphology and structure. The structure and morphology of TiO$_2$ were characterized by XRD and SEM, respectively. The photocatalytic activities were examined by the photodegradation of methylene blue (MB) under ultraviolet light ($\lambda$ ... = 365 nm) irradiation. The results indicated that the TiO$_2$ photocatalyst, using indocalamus leaves as templates, exhibited better adsorption and photocatalytic performance in degrading MB than using malus micro malus leaves, when the amount of nitric acid was 20 mL and following heat treatment at 600 °C.

Keywords: natural template; TiO$_2$; special morphology; photocatalysts

1. Introduction

In recent years, the preparation of nano-TiO$_2$ photocatalyst materials by template method has attracted the attention of researchers at home and abroad, because of its simple experimental device and operation, and the advantages of accurately controlling the morphology and structure of nanomaterials and effectively controlling the agglomeration phenomenon of nanomaterial [2], Thus has become a research hotspot. The biological template method mainly uses the highly complex and orderly spatial structure of natural biological materials to prepare materials that can reproduce the special structures capable of complex biological structures. There are many kinds of biological templates reported in the literature, including microbial templates (unicellular microorganisms, algae, bacteria, etc.) [3-6], Animal template (insect and insect wings, animal fur, etc.) [7-11], Plant template (cotton, petals, pollen, etc.) [12-15], Or other forms of the native cellulose template [16-18]. Because natural cellulose is widely found in natural plants and animals, the raw materials are cheap and easy to obtain, so the templates prepared by such templates have the characteristics of green environmental protection, low cost and simple operation.

In this paper, the morphology control and photocatalytic properties were studied. Xifu crabapple leaves and reed leaves are using nitric acid treatment, dredge vascular bundle in the vein to obtain natural cellulose template, butyl titanate in the solution can be uniformly distributed to the blade cells, then after high temperature calcination to remove organic matter such as leaves, can get a large porosity, high specific surface area of mesh structure of TiO$_2$ photocatalyst.

2. Experimental section

2.1. Reagents and instruments

Butyl titanate (TBT), Tianjin Chemical Reagent 1; Anhydroethanol, Tianjin Fengchuan Chemical Reagent Technology Co., Ltd.; Nitric acid, Tianjin Chemical Reagent 1; Methylene blue, Tianjin Guangfu Fine Chemical Institute; Xifu Begonia leaves and zhu bamboo leaves, Tianjin area.

Field-emission SEM (FE-SEMLEO-1530), German LEO Elektronenmikroskopie; X-ray diffraction analysis of the Cu target ($\lambda$ 0.15406nm), Japan Rigaku Company; UV-Visible spectrophotometer (7230G), Shanghai Precision Scientific Instrument Co., Ltd.; Precision balance (FA2004), Shanghai Shun Hengping
2.2. Preparation of the heterogeneous TiO₂ photocatalyst

Add 30 mL of absolute ethanol into a beaker, add 5 mL of butyl titanate, and stir solution A for 30 min; put 20 mL of absolute ethanol and 20 mL of nitric acid (6 mol/L) solution into the beaker, and mix well to get solution B; Add prepare solution A to solution B, and stir quickly for 30 min to obtain TiO₂ sol. With deionized water to fresh Xifu Begonia leaves and zhu leaves surface dust wash clean, Cut off the blade edge, And cut and placed into TiO₂ sol, Seal immersion for 24 h at room temperature, The soaked leaves were separated from TiO₂ sol using a filter, Wash the surface with absolute ethanol 2 to 3 times, Dry at room temperature for 24 h; Then put the dry blade into the electric blast drying box, 80 ℃ constant temperature for 2 h, Finally, by placing the blade in a crucible, Put into the mafier furnace to a certain temperature for 2 h heat treatment for slow heating, Gray-white sheet TiO₂ photocatalyst can be obtained.

2.3. Characterization of the photocatalytic activity of the heterogeneous TiO₂ photocatalyst

Add 25 mL of methylene blue solution at 10 mg/L to a 95 mm diameter dish, weigh 0.1 g of alien TiO₂ powder into the dish and apply it to a UV lamp (30 W, λ = 365 nm) (see Figure 1). At regular intervals, the supernatant was taken, the absorbance of the alien TiO₂ powder at the maximum absorption wavelength was measured by a UV-visible spectrophotometer, and the photocatalytic decolorization rate of methylene blue solution was calculated by equation (1), and graphed.

\[ \eta = \frac{A_0 - A_t}{A_0} \times 100\% \]  

Where \( A_0 \) is the absorbance value of the dye characteristic absorption peak before the reaction; \( A_t \) is the dye absorbance value measured when.

3. Characterization and photocatalytic properties of the heterogeneous TiO₂ photocatalyst

3.1. Formation mechanism of heterogeneous TiO₂ photocatalyst morphology

Leaves are mainly composed of three parts, namely, leaf veins, leaf epidermis and mesophyll. The distribution of leaf veins on the leaf surface can be roughly divided into three kinds of veins: network veins, bifurcation veins and parallel veins. Xifu Begonia leaves are network veins, while zhu bamboo leaves are parallel veins. The organic and inorganic components inside the blade are transported through the vascular bundle pipeline, and the transportation power mainly depends on transpiration, cohesion (hydrogen bond force) and active transport (concentration difference). When the plant leaves are in contact with TiO₂ sol, the concentration of TiO₂ outside the leaves is higher than that of the vascular bundle, resulting in a concentration difference, and there are many hydroxyl groups that can form hydrogen bonds attached to the inner wall of the vascular bundle, so that TiO₂ sol can enter the vein with the vascular bundle. In addition, because TiO₂ sol contains nitric acid, it can ionize to produce hydrogen ions, and the existence of hydrogen ions can effectively inhibit the hydrolysis of titanate and butyl ester in...
the sol, so the butyl titanate entering the leaves will not immediately decompose when the water in the leaves, resulting in the blockage of the vein channel. Therefore, the heterogeneous TiO₂ photocatalyst produced by this preparation method can replicate the leaf internal structure very well. This provides sufficient favorable conditions for the TiO₂ photocatalyst to have a large specific surface area and porosity.

3.2. The ological features of TiO₂ and determination of optimal biological template

At different heat treatment temperatures, TiO₂ photocatalyst made from Xifu Begonia leaves and zhu bamboo leaves as templates see Figure 2. It can be seen from comparison that with the increase of heat treatment temperature, the appearance and morphology of TiO₂ photocatalyst has changed significantly.

As can be seen from Figure 2a-2d, when the leaves of Xifu Begonia are used as the template, With the increase of the heat treatment temperature from 500℃ to 650℃, The color of the TiO₂ samples was gradually changed from brown to off-white, And the powder becomes more fluffy, This indicates that an increase in the heat treatment temperature, Ability to effectively remove the organic matter from the template, It is conducive to obtain a more loose porous structure of the powder; While Figure 2e shows, The powder particles made with zhu bamboo leaves as templates have a smooth surface, Compared with the powder made at the same temperature Figure 2c, Particle feeling is more obvious; In Figure 2f, To compare the photocatalytic activity of TiO₂ prepared from Figure 2c of Xifu Begonia leaves and Figure 2e, As can be seen, The adsorption and photocatalytic activity of TiO₂ photocatalyst prepared with reed leaves as template were significantly higher than those of Xifu Begonia leaves. SEM morphology was analyzed in both samples, and the results are shown in Figure 3.
Figure 2. The morphological characteristics and photocatalytic activity test curves of the samples prepared under different conditions

It can be clearly seen from Figure 3a-3b that the morphology structure of the sample is mesh, the same as the internal network structure of the blade. Therefore, it can be inferred that TiO₂ sol can be transported into the blade, and finally the organic material in the blade can be removed by heat treatment, and TiO₂ photocatalyst with template morphology can be obtained. As can be seen in Figure 3b, the produced TiO₂ well reproduces the internal morphology structure of the Xifu Begonia leaves, evenly dispersing some smooth holes.

Figure 3c-3d shows that the TiO₂ also reproduces the parallel tubular morphology of the zhu leaves; Figure 3d clearly shows that the aperture at the sample fracture is arranged in parallel, which is very similar to the vein structure of the zhu leaves. This morphology greatly expands the specific surface area of TiO₂, and the specific surface area is tested. The BET results show that the specific surface area of this sample is 47.3 m²/g. From the BJH equation calculation, we concluded that the aperture distribution is mainly concentrated around 4.7 nm, which indicates that the sample is a typical mesoporous structure. Therefore, the TiO₂ photocatalyst made from the zhu bamboo leaves as the template has a good adsorption of the methylene blue molecules on the surface, and the methylene blue solution can reach about 40% at the end of the dark reaction (see Figure 2f).

3.3. Photocatalytic activity of TiO₂ tested with XRD analysis

Figure 4 shows the alien TiO₂ photocatalytic curve and the XRD map obtained with different heat treatment temperatures. As can be seen from FIG. 4a, the TiO₂ photocatalyst increases with the increase of the temperature of heat treatment; when the heat treatment temperature is 600 ℃, the TiO₂ is best; but when the heat treatment temperature continues to increase, the activity decreases significantly. This indicated that the TiO₂ photocatalyst effectively degraded the methylene blue molecules under the conditions of UV light irradiation, and that the appropriate heat treatment temperature could effectively increase the TiO₂ photocatalysis Activity of the agent.
According to Figure 4b, when the heat treatment temperature is 500°C, the anatase phase has been formed, but there is an impurity phase, called composite phase 1, and the highest relative strength of the main peak of the impurity phase; at 550°C, the anatase phase increases significantly to become the main crystal phase, and there is still an impurity phase, called composite phase 2; when the temperature reaches 600°C, the sample is mainly anatase phase, and the diffraction peak of the impurity phase is very weak. FIG. 4a and 4b show that the heat treatment temperature increases the formation of anatase phase, thus
improving its photocatalytic activity; but when the heat treatment temperature is too high, the particle size of TiO₂ will increase or the rutile phase, which reduces the photocatalytic activity. Therefore, 600°C is considered as the optimal heat treatment temperature under the experimental conditions.

4. Conclusion

(1) With different macro and microscopic shapes, the adsorption and photocatalytic activity of the parallel tubular TiO₂ made with the zhu bamboo leaves as the template is much higher than that of the TiO₂ photocatalyst made with the Xifu Begonia leaf as the template.

(2) The special-shaped TiO₂ photocatalyst made with the bamboo blade as the template is mainly anatase crystal structure after 600°C heat treatment, and has a large specific surface area and porosity, so it has the highest photocatalytic activity.

5. References


