Study on Photocatalytic Properties of TiO_2 with Special Morphology by Using Natural Template

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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 s tructure. The structure and morphology of TiO_2 were characlerized by XRD and SEM, respectively. The photocatalytic activities were examined by the photodegradation of methylene blue(MB)under ultraviolet light(λ…=365nm) iradiation. 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 ℃.

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 materials 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 (λ 0.15406nm), Japan Rigaku Company; UV-Visible spectrophotometer (7230G), Shanghai Precision Scientific Instrument Co., Ltd.; Precision balance (FA2004), Shanghai Shun Hengping

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Scientific Instrument Co., Ltd.; Desktop centrifuge (TG 18 G), Hunan Kaida Scientific Instrument Co., Ltd.; Electric blast drying box (101-1AB), Tianjin Tester Instrument Co., Ltd.; Specific surface and aperture distribution analyzer, Conata Instruments, USA.

2.2. Preparation of the heterogeneous TiO_2 photocatalyst

Add 30 mL of absolute ethanol into a beaker, add 5 mL of butyl titanate, and stir solution A for 30min; put 20 mL of absolute ethanol and 20 mL of nitric acid (6mol / L) solution into the beaker, and mix well to get solution B; Add prepare solution A to solution B, and stir quickly for 30min to obtain TiO_2 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 TiO_2 sol, Seal immersion for 24h at room temperature, The soaked leaves were separated from TiO_2 sol using a filter, Wash the surface with absolute ethanol 2 to 3 times, Dry at room temperature for 24h; Then put the dry blade into the electric blast drying box, 80 ℃ constant temperature for 2h, Finally, by placing the blade in a crucible, Put into the mafer furnace to a certain temperature for 2h heat treatment for slow heating, Gray-white sheet TiO_2 photocatalyst can be obtained.

2.3. Characterization of the photocatalytic activity of the heterogeneous TiO_2 photocatalyst

Add 25 mL of methylene blue solution at 10mg / L to a 95mm diameter dish, weigh 0.1g of alien TiO_2 powder into the dish and apply it to a UV lamp (30W, λ =365nm) (see Figure 1). At regular intervals, the supernatant was taken, the absorbance of the alien TiO_2 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.

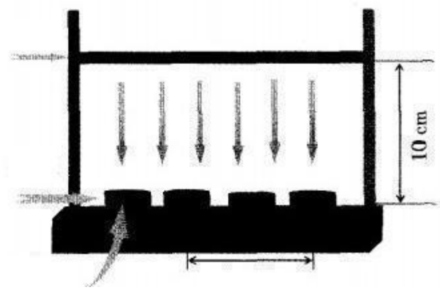

Figure 1. A Schematic diagram of the photocatalytic degradation experimental device

$$\eta = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

Where A_0 is the absorbance value of the dye characteristic absorption peak before the reaction; A is the dye absorbance value measured whent.

3. Characterization and photocatalytic properties of the heterogeneous TiO_2 photocatalyst

3.1. Formation mechanism of heterogeneous TiO_2 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 TiO_2 sol, the concentration of TiO_2 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 TiO_2 sol can enter the vein with the vascular bundle. In addition, because TiO_2 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

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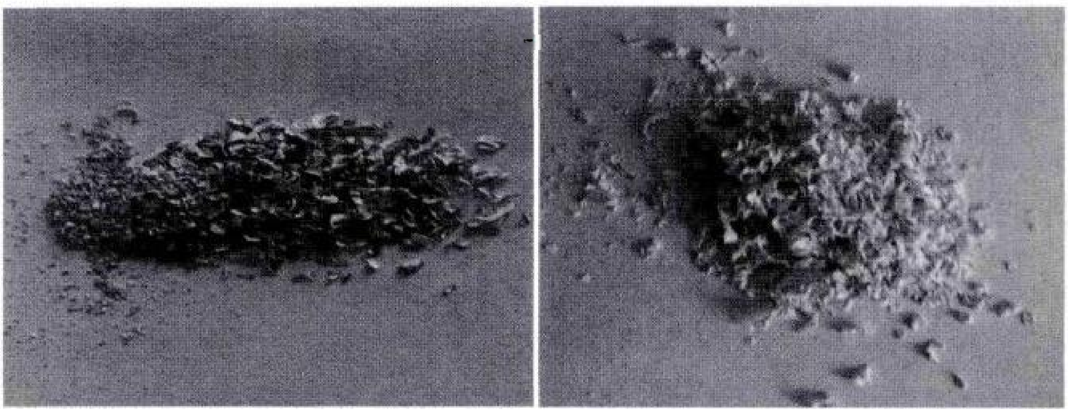
the sol, so the butyl titanate entering the leaves will not immediately decompose when the water in the leaves, resulting in the blockage of the vein channel. Therefore, the heterogeneous TiO_2 photocatalyst produced by this preparation method can replicate the leaf internal structure very well. This provides sufficient favorable conditions for the TiO_2 photocatalyst to have a large specific surface area and porosity.

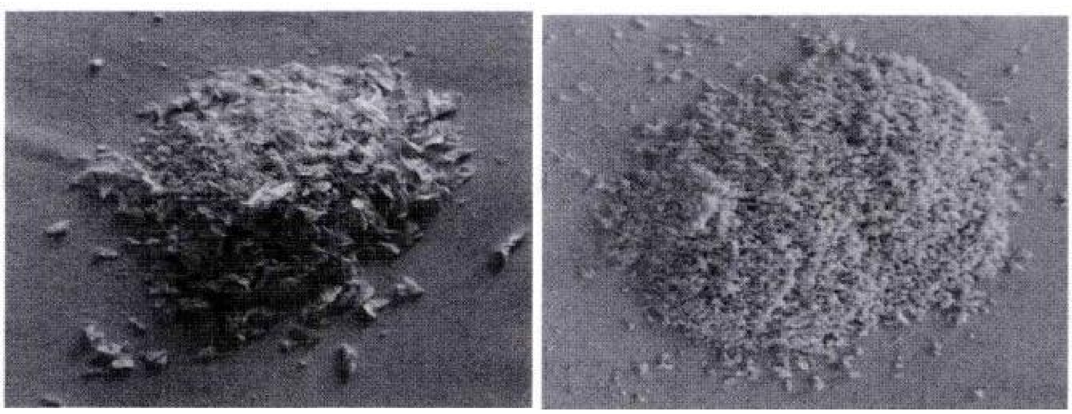
3.2. The ological features of TiO_2 and determination of optimal biological template

At different heat treatment temperatures, TiO_2 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 TiO_2 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 TiO_2 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 TiO_2 prepared from Figure 2c of Xifu Begonia leaves and Figure 2e, As can be seen, The adsorption and photocatalytic activity of TiO_2 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.



(a) Xifu Begonia leaf (500℃) (b) Xifu Begonia leaf (550℃)



(c) Xifu Begonia leaf (600℃) (d) Xifu Begonia leaf (650℃)

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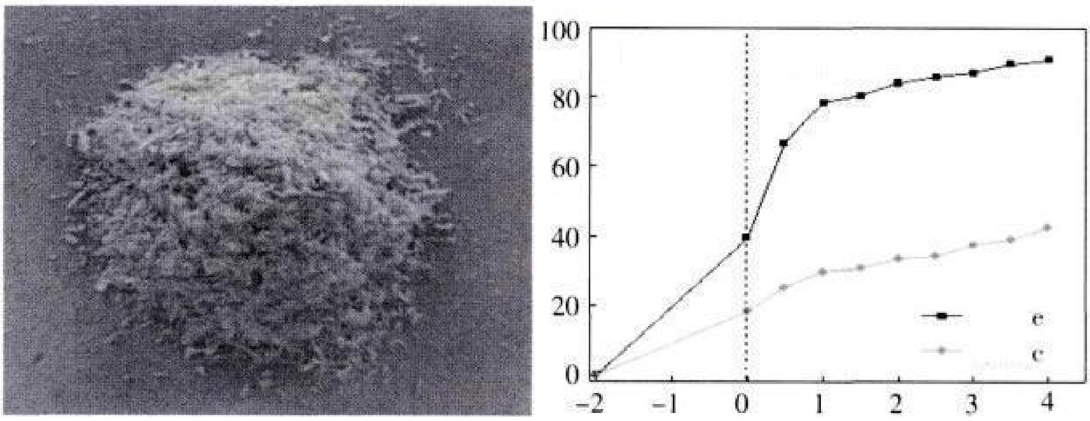

(e) zhu bamboo leaves (600°C) (f) Photocatalytic activity test curve of two samples

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 TiO_2 sol can be transported into the blade, and finally the organic material in the blade can be removed by heat treatment, and TiO_2 photocatalyst with template morphology can be obtained. As can be seen in Figure 3b, the produced TiO_2 well reproduces the internal morphology structure of the Xifu Begonia leaves, evenly dispersing some smooth holes.

Figure 3c-3d shows that the TiO_2 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 TiO_2, and the specific surface area is tested. The BET results show that the specific surface area of this sample is 47.3m/g. From the BJH equation calculation, we concluded that the aperture distribution is mainly concentrated around 4.7nm, which indicates that the sample is a typical mesoporous structure. Therefore, the TiO_2 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 TiO_2 tested with XRD analysis

Figure 4 shows the alien TiO_2 photocatalytic curve and the XRD map obtained with different heat treatment temperatures. As can be seen from FIG. 4a, the TiO_2 photocatalyst increases with the increase of the temperature of heat treatment; when the heat treatment temperature is 600℃, the TiO_2 is best; but when the heat treatment temperature continues to increase, the activity decreases significantly. This indicated that the TiO_2 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 TiO_2 photocatalysis Activity of the agent.

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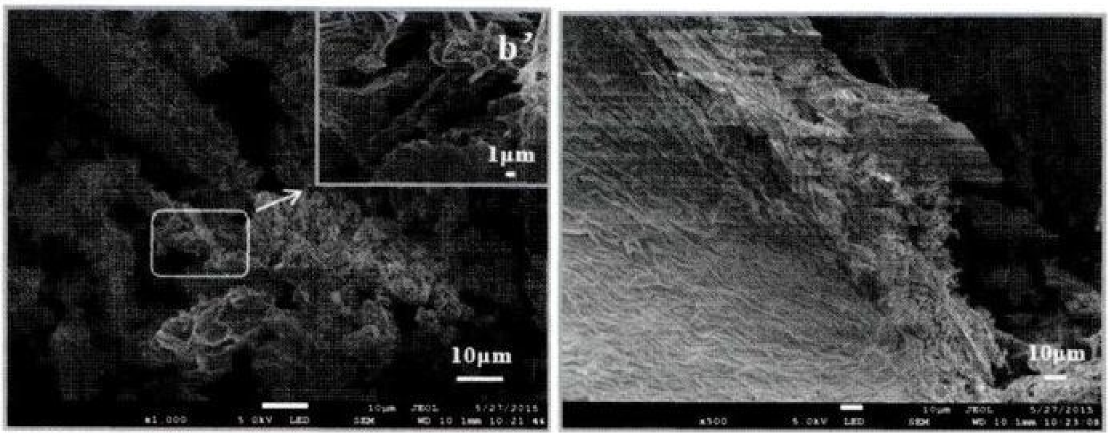
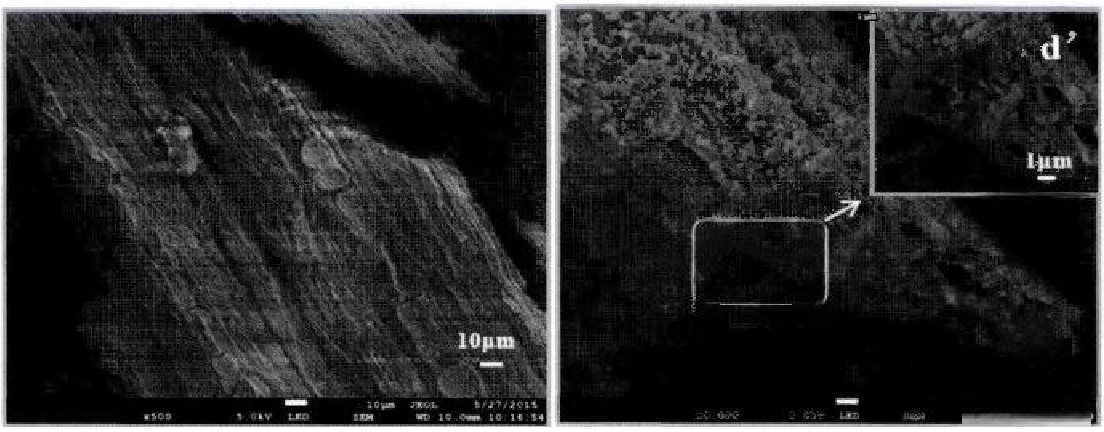


(a) Leaves of Xifu Begonia (b) Local amplification and further amplification of Xifu Begonia leaves



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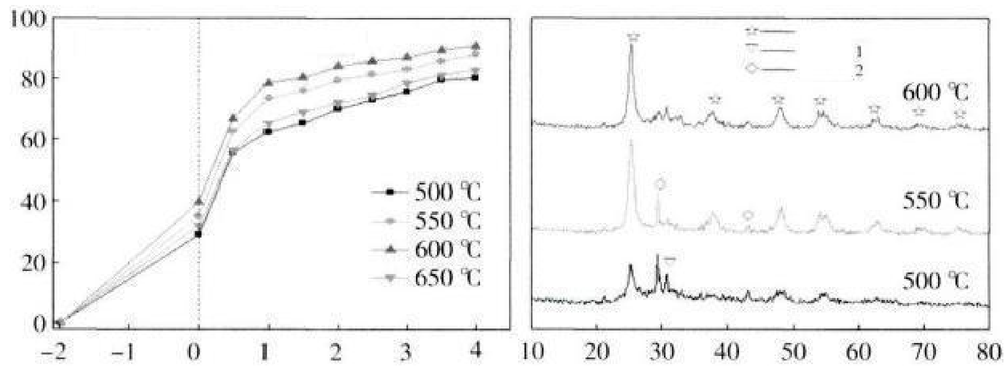
(c) zhu leaves (d) Local amplification and further amplification of zhu leaves

Figure 3 The SEM plots of the TiO_2 photocatalyst prepared from the different templates



(a) Photocatalytic curve (b)XRD

Figure 4 Alien TiO produced at different heat treatment temperatures, photocatalytic curve and XRD map

According to Figure 4b, when the heat treatment temperature is 500℃, 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℃, 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℃, 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

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improving its photocatalytic activity; but when the heat treatment temperature is too high, the particle size of TiO_2 will increase or the rutile phase, which reduces the photocatalytic activity. Therefore, 600℃ 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 TiO_2 made with the zhu bamboo leaves as the template is much higher than that of the TiO_2 photocatalyst made with the Xifu Begonia leaf as the template.

(2) The special-shaped TiO_2 photocatalyst made with the bamboo blade as the template is mainly anatase crystal structure after 600℃ heat treatment, and has a large specific surface area and porosity, so it has the highest photocatalytic activity.

5. References

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