# Glass fiber load optimization of the preparation and characterization of $TiO_2$ photocatalytic materials

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**Abstract.** I using the sol-gel/immacing jacquard to load $TiO_2$ film on the fiberglass. Through orthogonal test, the photocatalytic performance of the photocatalytic degradation of nitrobenzene wastewater by the loading $TiO_2$ was investigated, including the ratio of glue solution, the calcination temperature, the calcination time and the number of times of coating. The best condition of preparation of glass fiber load titanium dioxide thin film is: ethanol: water: the molar ratio of nitrate 10:6:1, calcination temperature is 450 ℃, calcination time is 90 minutes, coating number 4 times.The repeated test results showed that under the optimal preparation conditions, the degradation rate of nitrobenzene with a concentration of 40mg/L was up to 93.4%. The catalyst can be reused. The results of electron microscopy showed that the catalyst on the surface of glass fiber was evenly distributed in a tubular shape. The XRD resulted show that the crystal type of $TiO_2$ supported by glass fiber is sharp-titanium ore type with good photocatalytic performance.

## 1. Introduction

Since $TiO_2$ has a larger than surface area, it has high catalytic activity, high quantum effect, low energy consumption, no secondary pollution, degradation with photocatalytic, solar cells, sensors and so on., in such aspects as photoelectric catalysis, solar cells, sensor people's attention. $TiO_2$ due to its tiny particles, the preparation of prone to reunite phenomenon, use waste phenomena are prone to erosion, more difficult to recycle, and its response to narrow the scope of pure $TiO_2$ light quantum efficiency is low, serious constraints on its commercialization. Therefore, the preparation of high efficiency, stable and easy to recycle photocatalysts is a hot research topic. Glass fiber is a kind of excellent performance of inorganic non-metallic materials [4], for a variety of wavelengths of light have good pervious to light quality, as the carrier, after load can maximize the use of the energy of incident light, especially the use of the energy of sunlight; Relative to other carriers such as glass, glass fiber has a larger specific surface area, catalyst distribution are wrapped in the surface of carrier, can firmly adhere to the surface of the carrier, to enhance the catalytic reaction rate, and improve the treatment effect of wastewater; And glass fiber price is cheap, low cost, conducive to large-scale promotion.

The author by using glass fiber (GF) load $TiO_2$ catalyst has solved the traditional type photocatalyst powder processing wastewater after separation recycling difficult, cause the problem of waste, save energy, do not cause secondary pollution. The photocatalytic performance of the photocatalytic degradation of nitrobenzene wastewater by the loading $TiO_2$ was investigated by orthogonal test.

## 2. Test section

*2.1 Reagents and instruments*

Main equipment is: Test used ultraviolet-visible spectrophotometer (UV-9100), Acidity meter (HI98127) , Thermostatic drum wind drying oven（DHG-9140A）, Muffle furnace (HH-4) , Ultrasonic cleaning machine (KQ - 1004), Ultraviolet germicidal lamp (40 w)

Main reagents and drugs:30% H2O2 ,N-tetrabutyl titanate,Acetyl acetone,Nitric acid,Anhydrous ethanol,Concentrated sulfuric acid,Glass fiber,Nitrobenzene

*2.2 Preparation of glass fiber loaded $TiO_2$ film*

*2.2.1Glass fiber pretreatment*

Soak the prepared soft filamentous glass fiber with isopropanol and wash with ultrasonic for 15min. Then, the volume ratio of distilled water and hydrochloric acid solution was 2:1. Then soak in distilled water and wash with ultrasonic for 15min. Finally glass fiber with anhydrous alcohol immersion, ultrasonic cleaning for 15 minutes, after drying, under the condition of 105 ℃ heat storage 2 h, into the oven, and set aside.

*2.2.2 Preparation of glass fiber loaded $TiO_2$ film*

Sol-gel method [5, 7] was used for preparation. At room temperature, 30 ml of ethanol in the middle of 250 ml beaker, chase under magnetic stirring drop join 20 ml tetrabutyl titanate and 1.4 ml acetylacetone chelating agent,and keep the solution at a speed of 300 rad/min. After 30 minutes of magnetic stirring, the pale yellow transparent liquid is obtained.Meanwhile, anhydrous ethanol was prepared: water: mixed solution with a volume ratio of 10：4：1 of acetic acid. 0.05g of PEG was added under magnetic stirring, and transparent solution B was obtained after 15min. Add the B solution to the A solution slowly, and then mix it evenly. Continue to stir with magnetic force for 1 hour to form A transparent sol gel. Let stand at room temperature for 12 hours. Finally, the glass fiber loaded with $TiO_2$ was cooled to room temperature by soaking and pulping at low temperature, drying at normal temperature and calcining at high temperature.

*2.3 Test equipment and process*

The test device is shown in FIG. 1:

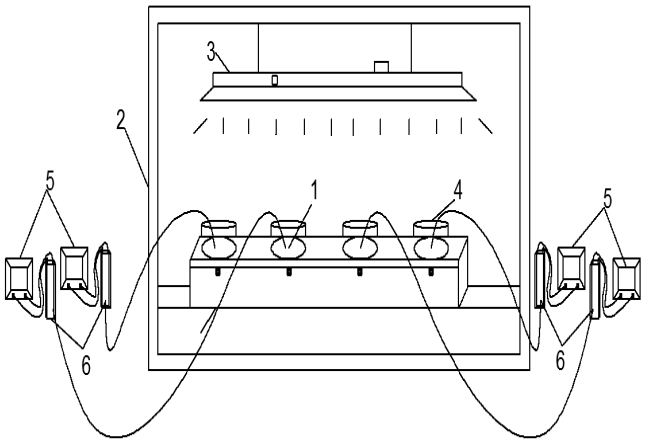


FIG.1 Photocatalytic reaction device.

Photocatalytic degradation was carried out in a self-made photocatalytic reactor. In order to eliminate interference from external light sources, the reactor adopted light-avoiding measures and operated the reaction in a dark box. A solution with 1000ml nitrobenzene concentration of 400mg/L and COD concentration of 100mg/L was placed in the middle of the reactor and irradiated by ultraviolet lamp. The catalyst samples were added with 0.15g, and the photoavoiding magnetic force was stirred for 30min. The catalyst was fully mixed to achieve adsorption-desorption equilibrium [6]. Sampling after open the light source, light stability 5 min, began to light reaction time, remember every 30 min sampling, sample under 4000 r/min, the centrifugal 15 min, take samples on determination of supernatant at 545 nm and 465 nm wavelength absorbance value, use after reaction and adsorption equilibrium solution's absorbance rate of nitrobenzene degradation rate and the removal rate of COD.

*2.4 Determination and characterization of photocatalytic performance of catalyst*

(1) The photocatalytic performance of supported photocatalyst TiO2/GF was evaluated by the degradation rate of nitrobenzene and the removal rate of COD. The concentration of nitrobenzene was determined by reduction-azo spectrophotometry [7].

(2) Scanning electron microscope (SEM) was used to observe the surface morphology of supported photocatalyst $TiO_2$/GF. The SEM analysis and observation of the samples were carried out after gold ion sputtering by the adhesive platform and ion sputtering instrument.

## 3. Results and discussion

*3.1 Optimized preparation of catalyst*

Orthogonal test design: the design of experiment with four factors three levels to investigate catalyst preparation process of ethanol: water: the molar ratio of nitrate, calcining temperature, calcining time and the number of coating for catalyst inner defect location and the influence of and the influence on its external crystal structure, thus affecting the activity of photocatalyst.

Table 1 Orthogonal design table of factor conditions.

| | **Values of various factors** | | | |
|---|---|---|---|---|
| **Level** | **Calcination time（h）** | **Ethanol: water: molar ratio of nitric acid** | **Number of coating** | **Calcination temperature（℃）** |
| 1 | 1.5 | 4：3：1 | 2 | 400 |
| 2 | 2 | 10：6：1 | 3 | 450 |
| 3 | 2.5 | 2：1：1 | 4 | 500 |

Orthogonal test analysis: the final sampling centrifugation was performed after 2h of photocatalytic reaction. The orthogonal test results and data processing results are shown in table 2. Through the analysis of the range R, the higher the R value is, the greater the influence of this factor on the test results. Results show that all the factors impact on the catalyst photocatalytic performance of the primary and secondary sequence as follows: ethanol: water: the molar ratio of nitrate calcination temperature (℃) > coating times >calcining temperature (℃) > calcination time. Through the analysis of variance, there were various influencing factors of the optimal preparation conditions: ethanol: water: the molar ratio of nitrate as the 10:6:1, calcination temperature is 450 ℃, calcination time was 90 min, coating times for 3 times, nitrobenzene wastewater degradation rate was 93.4%.

Table 2 Orthogonal test results.

| NO. | Values of various factors | | | | Degradation rate（%） |
|---|---|---|---|---|---|
| | Calcination time（h） | Ethanol: water: molar ratio of nitric acid | Number of coating | Calcination temperature（℃） | |
| 1 | 1.5 | 4：3：1 | 2 | 400 | 65.2 |
| 2 | 1.5 | 10：6：1 | 3 | 450 | 93.4 |
| 3 | 1.5 | 2：1：1 | 4 | 500 | 41.6 |
| 4 | 2 | 4：3：1 | 4 | 400 | 57 |
| 5 | 2 | 10：6：1 | 2 | 450 | 74.1 |
| 6 | 2 | 2：1：1 | 3 | 500 | 55 |
| 7 | 2.5 | 4：3：1 | 3 | 400 | 48.2 |
| 8 | 2.5 | 10：6：1 | 4 | 450 | 68.5 |
| 9 | 2.5 | 2：1：1 | 2 | 500 | 60.6 |
| K1 | 200.02 | 170.4 | 188.7 | 199.9 | |
| K2 | 186.1 | 236 | 211 | 196.6 | |
| K3 | 177.3 | 1517.2 | 163.9 | 167.1 | |
| k1 | 66.73 | 56.8 | 62.9 | 66.63 | |
| k2 | 62.03 | 78.67 | 70.33 | 65.53 | |
| k3 | 59.1 | 52.4 | 54.63 | 55.7 | |
| R | 7.63 | 26.27 | 15.7 | 10.93 | |

*3.2Characterization analysis*

The loaded photocatalyst $TiO_2$/GF prepared under optimal conditions was analyzed by SEM under electron microscope, and the results were shown in FIG. 2.FIG. .3

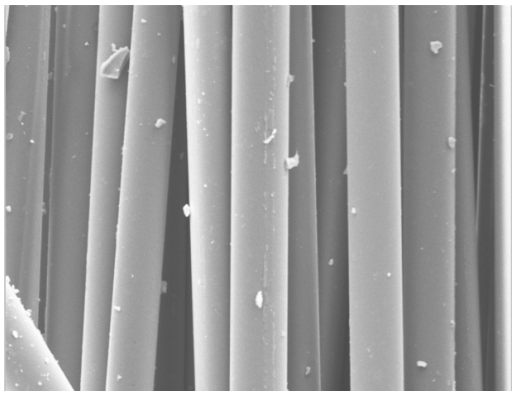

FIG. 2The surface of pure glass fiber under different SEM and the surface of glass fiber loaded with $TiO_2$.

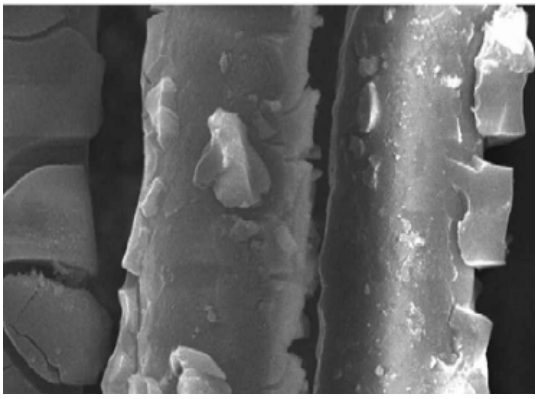

FIG. 3The surface of pure glass fiber under different SEM and the surface of glass fiber loaded with $TiO_2$.

According to the FIG. 2.FIG. .3electron microscopy (sem) analysis shows that $TiO_2$ in. Glass fiber surface distribution is uniform package, each root on glass fiber has a "trunk" of the distribution of catalyst, the surface of the carrier continuous compact, in addition to a small amount of cracked little holes appear fine lines. This distribution is beneficial to the contact between catalyst and pollutant as well as the utilization of ultraviolet light, and can improve the photocatalytic performance of catalyst. Generally, $TiO_2$ has three crystal types: Anatase (type A) and Rutile (R) [9]. Rutile $TiO_2$ is stable and compact compared with sharp titanium $TiO_2$, with high hardness, density, dielectric constant and refractive index, and high hiding and coloring power. And sharp titanium type of $TiO_2$ in the visible part of shortwave reflectivity is higher than $TiO_2$ rutile type, with blue color, and the ultraviolet absorption capacity, lower than the rutile type high photocatalytic activity than rutile type [10].

*3.3Photocatalytic performance analysis*

Benchmark test conditions: take 1000 ml water, nitrobenzene wastewater concentration of 40 mg/L, pH value of 3, add 1 ml/L plus 30% oxidant $H_2O_2$, under 40 w uv lamp radiation under the conditions of photocatalytic reactor, add 10 g/L of photocatalyst, aeration (0.8 $m^3$ / L), test reaction time is 3 h, every 30 min centrifugal nitrobenzene concentration sampling test. The removal rate of nitrobenzene from water samples was compared. Comparison of photocatalyst degradation effect is shown in figure 4:

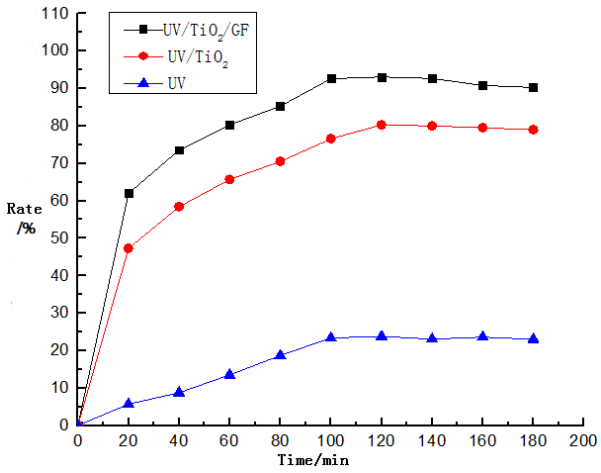


FIG. 4 The degradation effect of nitrobenzene wastewater under different conditions.

According to the figure 3 shows that under uv irradiation, the treatment effect of load type TiO2 / GF is best, followed by the pure TiO2, under the condition of no catalyst, simple ultraviolet irradiation

degradation rate is only 23.8%, lowest of glass fiber load more effectively improve the photocatalytic performance of the catalyst. Reason is that affect the catalyst activity is not only a number of catalyst itself, more lies in its distribution state and its contact with pollutants in the water surface area [6, 8], and carrier glass fiber has a larger contact surface area, larger specific surface area of the glass fiber load makes the catalyst has greatly increased, and catalyst on the surface of the glass fiber present package type load, and then make its contact with the water pollutants REDOX reaction is accelerated, increase its photocatalytic performance.

## 4. Conclusion

(1) Using sol-gel method $TiO_2$/GF, through orthogonal test that the preparation factors on the fiber glass load $TiO_2$ photocatalyst degradation of nitrobenzene wastewater effect as follows: the influence of ethanol: water: the molar ratio of nitrate > coating times> calcining temperature (℃) > calcination time.

(2) The best preparation conditions are: ethanol: water: the molar ratio of nitrate as the 10:6:1, calcination temperature is 450 ℃, calcination time was 90 min, the number of coating for 3 times. Under the optimal preparation conditions, $TiO_2$/GF had better degradation effect on nitrobenzene wastewater, with a degradation rate of 93.4%.

(3) The results of SEM analysis showed that $TiO_2$ was "tubular" wrapped around the glass fiber.

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