Photocatalytic Degradation of Methylene Blue Solution Using N-doped Titanium Dioxide Thin Film

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Abstract: Anhydrous ethanol 100 mL was measured and a certain amount of tetrabutyl titanate and acetylacetone were added to label as the base solution A, which was mixed evenly under the stirring of a magnetic stirrer. Anhydrous ethanol 50 mL was added with a certain amount of nitric acid and water, mixed evenly and labeled as base solution B. N-doped titanium dioxide films were mixed into liquid B with ammonia as the N source in a certain proportion. The reaction was stirred by a stirrer under the condition of chamber temperature, and the pH value of the basic solution A should be continuously controlled between 3 and 4, and the basic solution B should be slowly added to the basic solution A. After magnetically stirring the prepared sol for 10 min, slowly adding a certain amount of ammonia water, and then continuing to stir for 15 min, N-doped titanium dioxide sol was obtained. The molar ratio of control acetyl acetone, nitric acid, tetrabutyl titanate, water and anhydrous ethanol is = 1:1:5:25:150. The suitable degradation conditions of the films were studied, including calcination time of 50 min, calcination temperature of 450 ℃, coating layer number of 4, and molar ratio of ammonia water to tetrabutyl titanate of 1:25. The prepared N-doped titanium dioxide sol was plated on the pre-treated substrate by rotating method, dried under natural conditions, calcined in Muffle furnace, kept the furnace temperature at 5 ℃/min to 450 ℃, kept constant at 450 ℃ for 50 min, and then cooled to room temperature naturally, and the coating was completed once, and the above coating was repeated four times. N-doped titanium dioxide films prepared were used for photocatalytic degradation of methylene blue.

Keywords: N-doped Titanium Dioxide; Thin Film; Photocatalytic Degradation; Methylene Blue

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1 Introduction

Today, with the rapid development of industrialization, People's daily life, business and national defense are faced with environmental problems such as hazardous waste treatment, groundwater pollution and toxic air pollutant control [1-4]. Some advanced physico-chemical methods could eliminate pollution, for example, the photocatalytic method of semiconductor nano-titanium dioxide, which arose in the 20th century, could complement or complement traditional methods to eliminate or transform pollution caused by dangerous

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chemical wastes [5-8]. In the field of photocatalytic materials, titanium dioxide had been widely concerned because of its advantages of non-toxicity, no pollution, low cost and high reuse. Titanium dioxide as a green semiconductor material, it is also widely used in cosmetics, coatings, water pollution treatment and medical fields [9-11]. Because there are still some problems in the actual production and application of titanium dioxide, many scholars are making unremitting efforts to prepare the modified titanium dioxide with low cost, good effect, easy to collect and reuse, and to optimize its conditions [12-16]. Combined with the needs of actual production and daily life, the condition experiments of titanium dioxide prepared by sol-gel method were systematically studied. N-doped titanium dioxide films that could be easily reused by sol-gel method with ammonia water as nitrogen source, and conducted experimental studies on the condition of degradation with dyes as simulated wastewater. Hope to have some inspiration for people's actual life.

2 Experimental Part

2.1 Experimental Reagents

Anhydrous ethanol (analytically pure, Sinopharm Group Chemical Reagent Co.); Tetrabutyl titanate (chemically pure, Sinopharm Group Chemical Reagent Co., LTD.); Acetyl acetone (Analytically pure, Sinopharm Group Chemical Reagent Co., LTD.); Glacial acetic acid (analytical pure, Sinopharm Group Chemical Reagent Co., LTD.); Ammonia (pure analysis, Sinopharm Group Chemical Reagents Co., LTD.); Nitric acid (superior pure, Sinopharm Group Chemical Reagent Co., LTD.); Methyl blue (analytical pure, Sinopharm Group Chemical Reagent Co., LTD.).

2.2 Experimental Instruments

Hg-6 magnetic heating Agitator (Jintan Fuhua Instrument Co., LTD.); WS70-1 infrared fast dryer (Nantong Scientific Instrument Co., LTD.); PLS-LAM long arc mercury lamp (Beijing Changtuo Technology Co., LTD.); UV9600 ultraviolet Visible spectrophotometer (Beijing Rayleigh Analytical Instrument Company); SHZ-C type circulating water type multi-purpose vacuum pump, (Henan Gongyi Yingyu Yuhua Instrument Co., LTD.); PLS type photochemical reaction system (Beijing Pofeilai Technology Co., LTD.); PHS-10A digital acidity/ion meter, Xiaoshan Scientific Instrument Co., LTD.); SRJX box type electric furnace (Beijing Rayleigh Analytical Instrument Company).

3 Preparation of N-doped Titanium Dioxide Thin Films

3.1 Preparation of N-doped Titania Sol

N-doped titanium dioxide sol was prepared. Anhydrous ethanol 100 mL was measured and a certain amount of tetrabutyl titanate and acetylacetone were added to label as the base solution A, which was mixed evenly under the stirring of a magnetic stirrer. Anhydrous ethanol 50 mL was added with a certain amount of nitric acid and water, mixed evenly and labeled as base solution B. N-doped titanium dioxide films were mixed into liquid B with ammonia as the N source in a certain proportion. The molar ratio of control acetyl acetone, nitric acid, tetrabutyl titanate, water and anhydrous ethanol is = 1:1:5:25:150. The reaction was stirred by a stirrer under the condition of chamber temperature, and the pH value of the basic solution A should be continuously controlled between 3 and 4, and the basic solution B should be slowly added to the basic solution A. After magnetically stirring the prepared sol for 10 min, slowly adding a certain amount of ammonia water, and then continuing to stir for 15 min, N-doped titanium dioxide sol was obtained.

3.2 Preparation of N-doped Titanium Dioxide Thin Films

In the experiment, silica slide was selected as the substrate for coating. Before coating, the slide should be pre-treated. First, the substrate should be soaked in the mixture of hydrochloric acid and ethanol for 24 h, cleaned in distilled water for 3 times after removal, cleaned in ultrasonic cleaner for 30 min, cleaned in distilled water for 3 times after removal, and dried in a blast dryer. The pre-treated slides were rotated and coated in N-doped titanium dioxide sol, dried under natural conditions and calcined in Muffle furnace. The furnace temperature was kept at 5 ℃/min to 450 ℃, and after constant temperature at 450 ℃ for 50 min, they were naturally cooled to room temperature and taken out, the coating was completed once. If multiple coatings were needed, repeat the above.

3.3 XRD Characterization of Titanium Dioxide

The titanium dioxide prepared under the above suitable experimental conditions was characterized by XRD. It could be seen from Figure 1 that a strong (101) plane diffraction peak of anatase phase appeared near 2θ = 25.3°, indicating that anatase type titanium dioxide with small particle size had been prepared and had better thermal stability at higher temperatures. The XRD pattern was compared with the standard X-ray diffraction card, which further indicated that the prepared anatase type titanium dioxide was obtained. In addition, the observation of peak peak and peak height indicated that anatase type titanium dioxide with small particle size was formed.

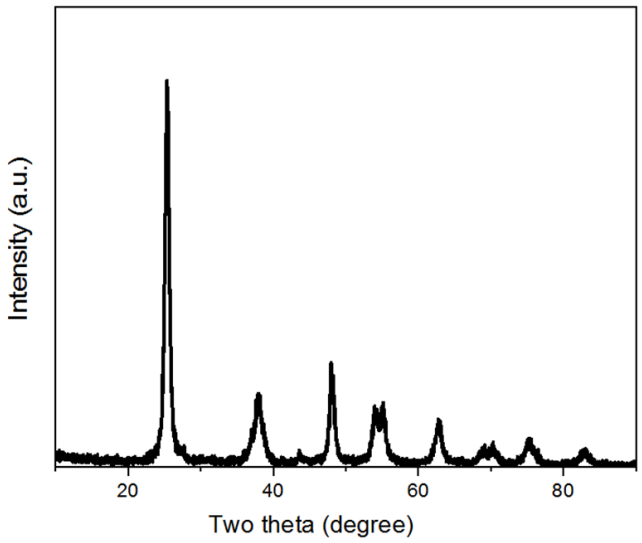

Figure 1 XRD pattern of titanium dioxide

4 Results and Discussion

Because of its high photocatalytic activity, titanium dioxide has been widely used in the field of sewage treatment. The experiment used methylene blue solution as a simulated wastewater to verify the photocatalytic performance of the sol prepared by the experiment after coating and burning on the surface of silicon dioxide.

4.1 Effect of Calcination Time on Degradation Rate

The prepared N-doped titanium dioxide sol was plated on the pre-treated substrate by rotating method, dried under natural conditions, calcined in Muffle furnace, kept the furnace temperature at 5 ℃/min to 450 ℃, kept constant at 450 ℃ for 50 min, and then cooled to room temperature naturally, the coating was completed once, and the above coating was repeated four times. N-doped titanium dioxide films prepared were used for photocatalytic degradation of methylene blue.

It could be seen from Figure 2 that the degradation rate of methylene blue catalytic degradation gradually increased with the increase of calcination time. When the calcination temperature was below 50 min, because the calcination time was too short, titanium dioxide mainly existed in the form of amorphous, anatase crystal type was not completely formed, so the degradation rate was small. With the increase of calcination time, anatase crystal form gradually formed and degradation rate increased. When the calcination time was 50 min or more, anatase crystal form was completely formed and the degradation rate was the highest. At the same time, the stable combination of titanium dioxide and substrate was conducive to re-coating and reuse, so the calcination time of N-doped titanium dioxide film was selected for 50 min in the experiment.

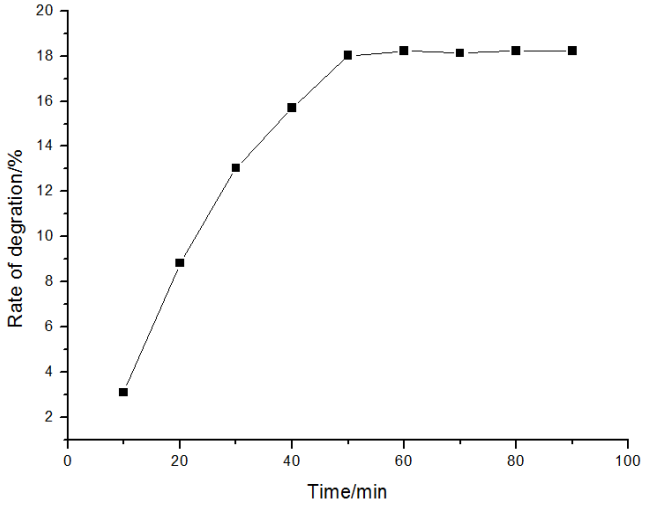

Figure 2 Effect of calcination time on degradation rate

4.2 Effect of Calcination Temperature on Degradation Rate

The prepared N-doped titanium dioxide sol was plated on the pre-treated substrate by rotating method, dried under natural conditions, calcined in Muffle furnace, kept the furnace temperature at 5 ℃/min from 100 ℃ to 600 ℃, kept at constant temperature for 50 min, cooled to room temperature, and repeated the

above coating for 4 times. N-doped titanium dioxide films prepared were used for photocatalytic degradation of methylene blue.

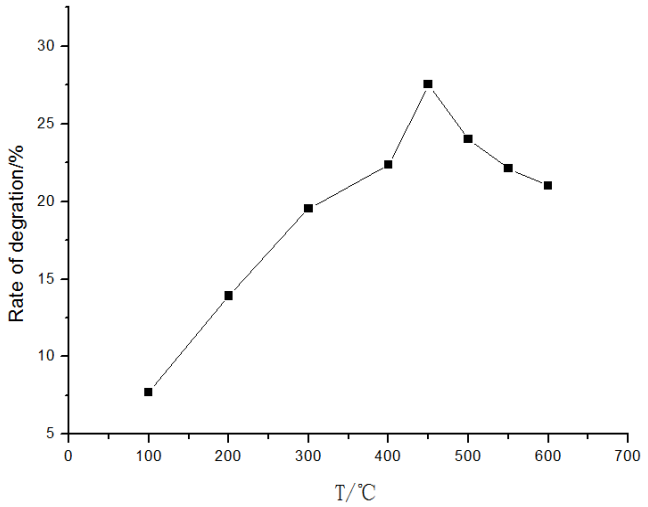

Figure 3 Effect of calcination temperature on degradation rate

As could be seen from Figure 3, from 100 ℃ to 450 ℃, the degradation rate of catalytic degradation of methylene blue gradually increased with the increase of temperature, and the maximum degradation rate was reached when the temperature reached 450 ℃. When the temperature continued to rise, the degradation rate gradually decreased. This was because when the temperature was low, the crystal type of titanium dioxide was amorphous, and with the increase of temperature, the crystal type of titanium dioxide was gradually transformed from amorphous to anatase, and the degradation rate of anatase crystal titanium dioxide was the largest, so the degradation effect was gradually better. As the temperature continued to rise, anatase crystal type gradually changed into rutile type at higher temperature. The degradation effect of rutile type titanium dioxide was slightly lower than that of anatase type. When the temperature was above 450 ℃, the degradation rate of methylene blue simulated pollutants decreased. Therefore, the calcination temperature of N-doped titanium dioxide film was 450 ℃.

4.3 Effect of Coating Times on Degradation Rate

The prepared N-doped titanium dioxide sol was plated on the pre-treated substrate by rotating method, and then dried in the Muffle furnace under natural conditions for calcination. The furnace temperature was kept at 5 ℃/min to 450 ℃, and after constant temperature at 450 ℃ for 50 min, it was naturally cooled to room temperature and taken out, the coating was completed once, and the above coating was repeated 1 to 10 times. N-doped titanium dioxide films prepared were used for photocatalytic degradation of methylene blue.

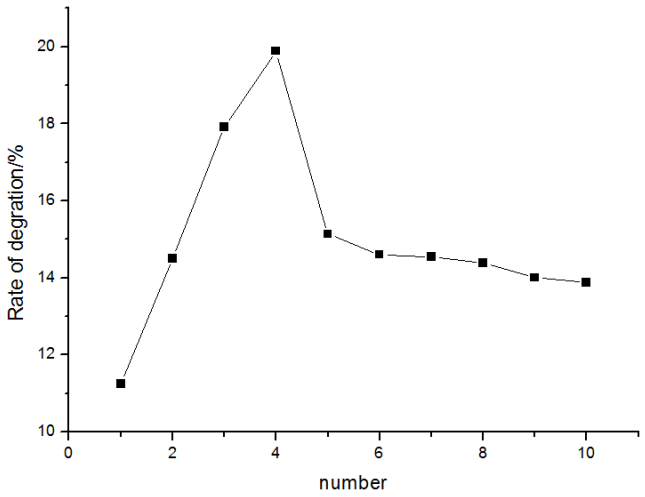

Figure 4 Effect of coating times on degradation rate

As could be seen from Figure 4, when the N-doped titanium dioxide coating ranged from 1 to 4 layers, the degradation rate of catalytic degradation of methylene blue gradually increased with the increase of the number of N-doped titanium dioxide coating layers, and the degradation rate reached the maximum when the number of coating layers was 4. With increasing the number of coating layers, the degradation rate of methylene blue decreased gradually. This was because titanium dioxide excited photogenerated electron hole pairs when it was irradiated by light, which played an important role in photocatalytic degradation. When the number of coating layers increased gradually, the photogenerated electron hole pairs generated by titanium dioxide films increased correspondingly, so the degradation rate of methylene blue catalytic degradation increased gradually. When the N-doped titanium dioxide coating was more than 4 layers, the number of coating layers increased gradually, and the degradation rate of methylene blue catalytic degradation decreased gradually. This was because when the number of coating layers gradually increased to more than 4 layers, the adsorption of particles by the coating layer was reduced, and the effective specific surface area was also reduced, which affected the photogenerated electron hole pairs at the base layer, so the catalytic

degradation rate was reduced. Therefore, the number of N-doped titanium dioxide coating layers was chosen as 4 in the experiment.

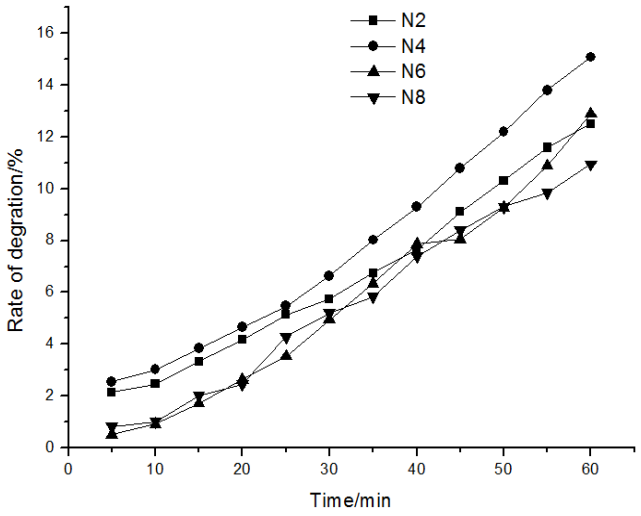

Figure 5 Effect of different content N-doped on degradation rate

4.4 Effect of Different Content N-doped on Degradation Rate

Titania sol with different content N-doped was prepared. In the experiment, ammonia was selected as the nitrogen source, and the molar ratio of ammonia and tetrabutyl titanate was 1:50, 1:25, 3:50 and 2:25 to prepare the sol with different content N-doped. The coating method was applied on the substrate and repeated for 4 times. The photocatalytic degradation of methylene blue by prepared titanium dioxide films with different content N-doped was studied.

According to Figure 5, titanium dioxide with different content N-doped had an effect on the degradation rate of methylene blue. The optimum content N-doped of titanium dioxide was 1:25 molar ratio of ammonia and tetrabutyl titanate, and the photocatalytic degradation rate was the best. When the amount of ammonia was too small, the nitrogen element entered the titanium dioxide lattice less, which had little effect on the photocatalytic degradation rate. The photocatalytic degradation rate increased with the addition of ammonia. However, the more nitrogen added, the better the catalytic effect. When the amount of ammonia added exceeds 1:25, the photocatalytic degradation rate decreased. The reason might be that the photocatalytic activity was changed by other influences on the titanium dioxide lattice, and the addition of too much ammonia water would make the sol easy to hydrolysis or shorten the gel time, which was not conducive to the coating. Therefore, the suitable doping amount in the experiment was the molar ratio of ammonia water and tetrabutyl titanate substance 1:25. By doping titanium dioxide crystals, the energy required for electron excitation could be reduced by introducing impurity levels and defect levels into the band gap, and the spectral response range of titanium dioxide could be extended to the visible region. Previous studies mainly focused on the doping of metal ions, the introduction of metal ions was easy to form a carrier recombination center and reduce the photocatalytic efficiency. Doping an appropriate amount of N could form a new hybrid energy level, narrow the band gap width of titanium dioxide, enhance the absorption of visible light, and become a shallow potential trapping trap for photogenerated electrons and holes, reduce the recombination rate of electron hole pairs, improve the efficiency of light quantization, and enhance the photocatalytic activity.

5. Conclusions

The conditions of preparation of titanium dioxide by sol-gel method were optimized and the suitable conditions were determined. The experimental conditions of the formation time of titania gel by sol-gel method included the amount of water added, the amount of nitric acid catalyst, the choice and amount of chelating agent, the choice and amount of solvent, the hydrolysis temperature and other experimental factors.

N-doped titanium dioxide films were prepared by sol-gel method. The suitable degradation conditions of the films were studied, including calcination time of 50 min, calcination temperature of 450 ℃, coating layer number of 4, and molar ratio of ammonia water to tetrabutyl titanate of 1:25. The prepared N-doped titanium dioxide sol was plated on the pre-treated substrate by rotating method, dried under natural conditions, calcined in Muffle furnace, kept the furnace temperature at 5 ℃/min to 450 ℃, kept constant at 450 ℃ for 50 min, and then cooled to room temperature naturally, and the coating was completed once, and the above coating was repeated four times. N-doped titanium dioxide films prepared were used for photocatalytic degradation of methylene blue.

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