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# *Research on Preparation and Photocatalytic Performance of Nitrogen-doped Titanium Oxides*

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***Keywords:*** Sol-gel Method, Titanium Dioxide, Nitrogen Doping, Methyl Orange Dye, Degradation Rate

***Abstract:*** With butyl titanate as the titanium source, stronger ammonia water as the nitrogen source, glacial acetic acid as the catalyst, and absolute ethyl alcohol as the solvent, this research prepares pure titanium dioxide ($TiO_2$) and nitrogen-doped $TiO_2$ samples by sol-gel method. Furthermore, taking the degradation rate of methyl orange dye as the evaluation index, this research examines the influence exerted by nitrogen-doped $TiO_2$ samples on the degradation performance of methyl orange dye. Concurrently, such methods as X-ray diffractometer and ultraviolet-visible spectrophotometer are employed to characterize the samples. In this foundation, this research investigates the effects of diverse annealing temperatures on nitrogen-doped $TiO_2$ samples. Findings from catalytic degradation experiments reveal that nitrogen-doped $TiO_2$ samples annealed at 400 °C exhibit excellent photocatalytic performance.

## 1. Introduction

The textile industry typically discharges excessive amounts of azo dye wastewater pollutants annually. Improper treatment of these pollutants may cause them to enter the human body and induce canceration of human cells, eventually seriously endangering human health [1]. Particularly, methyl orange dye is regarded as one of the most common azo pollutants within the textile industry. In this connection, one of the most potential materials for degrading such pollutants is the catalytic material represented by titanium dioxide ($TiO_2$) [2]. In comparison with other metal oxides, $TiO_2$ is widely applied in the catalytic degradation of pollutants by virtue of its excellent physical-chemical properties, non-toxicity, and low price [3]. The $TiO_2$, however, contains anatase with a large forbidden bandwidth and a band gap energy of 3.2 eV, solely exhibiting photocatalytic activity under ultraviolet irradiation. Consequently, its photocatalytic application in visible light is limited [4]. To address the defects of photo-induced electron-hole recombination, low quantum efficiency, and insufficient utilization of solar energy exposed by $TiO_2$ catalyst during the photocatalytic process [5], extensive researchers have made considerable efforts to improve the catalytic performance of $TiO_2$, proposing various modification methods such as precious metal deposition [6], semiconductor recombination [7], ion doping [8], and surface photosensitization [9].

Regarding ion doping, rare earth ion doping serves as one of the effective modification methods, which is capable of improving the adsorption and degradation ability of $TiO_2$ to organic pollutants. Moreover, while promoting the redshift of the optical absorption edge of $TiO_2$, reducing the ineffective recombination of photo-induced carriers, and enhancing the adsorption capacity of the catalyst, appropriate rare earth ion doping is beneficial to inhibit the phase transition from anatase to rutile, thereby improving the photocatalytic activity. In this regard, this research investigates the effects of different annealing temperatures on the photocatalytic degradation of methyl orange dye by N-doped $TiO_2$ samples.

## 2. Experimental Section

### 2.1. Reagents and Instruments

Reagents include butyl titanate, stronger ammonia water, absolute ethyl alcohol, methyl orange dye, glacial acetic acid, and analytical reagent purchased from Ruilite (Tianjin) Experimental Consumables Sales Co., Ltd.

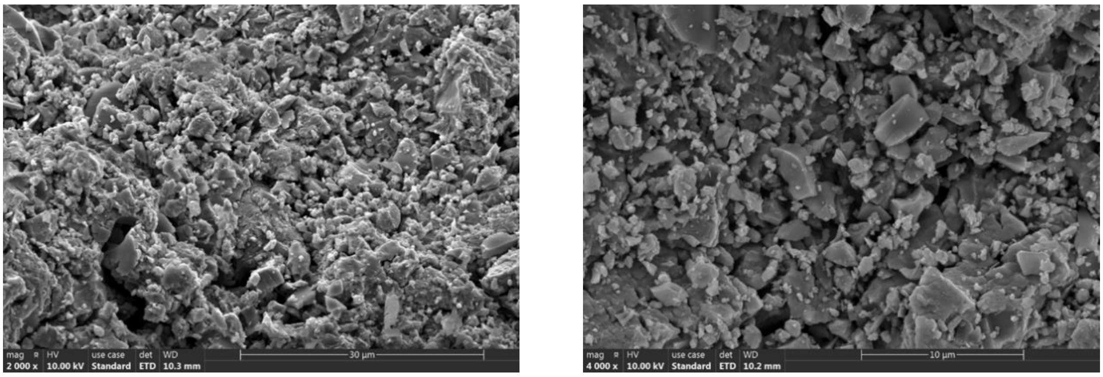
Instruments are as follows: *a)* heat-gathering constant-temperature heating magnetic stirring apparatus (DF-101S, Gongyi Yuhua Instrument Co., Ltd.); *b)* muffle furnace (STM-6-17, Henan Sante Furnace Technology Co., Ltd.); *c)* xenon-lamp light source system (PLS-SXE300+, Beijing Perfectlight Technology Co., Ltd.); *d)* electronic balance (JJ224BC, G&G Measurement Plant); *e)* ultraviolet-visible spectrophotometer (UV-VIS, UV-2700, Daojin Instrument Co., Ltd.); and, *f)* X-ray diffractometer (XRD, XD6, Beijing Purkinje General Instrument Co., Ltd.).

### 2.2. Sample Preparation

Concretely, to begin with, 10 ml of butyl titanate was slowly added into 40 ml of absolute ethyl alcohol dropwise, with 5 ml of stronger ammonia water being added later. During this process, the reagents above were dripped and stirred with a magnetic stirrer to prepare a solution, which was left standing to form a stable and uniform transparent sol. Subsequently, the above sol was aged for 24 hours to form a gel, which was dried at a temperature of 100 ℃ and ground into powder. Lastly, the powdered gel was annealed at different temperatures for 1 hour to prepare N-doped $TiO_2$ powder. Notably, the annealing temperature was changed during the preparation process. In other terms, annealing was implemented at 300 ℃, 400 ℃, 500 ℃, 600 ℃, and 700 ℃, respectively, to explore the influence exerted by different annealing temperatures on the doping performance.

## 3. Results and Discussion

### 3.1. Scanning Electron Microscope Analysis



(a) (b)

Figure 1: SEM Images of $TiO_2$(a)and N- $TiO_2$ (b)Samples.

The particle morphology of $TiO_2$ and samples annealed at 400°C (i.e., N-$TiO_2$-400 ℃) was observed by scanning electron microscope (SEM). As can be seen from Figure 1, the doping of nitrogen facilitates the uniform and flat particle size distribution of $TiO_2$ as well as the reduction of agglomeration phenomenon.

### 3.2. XRD Analysis

Figure 2 depicts N-doped $TiO_2$ samples at different annealing temperatures. As can be observed from Figure 2, with the increase in annealing temperature, the crystal structure of the sample changes in the crystalline phase. More precisely, the sample displays an amorphous phase at 300 °C, an anatase phase at 400 °C, and a rutile-anatase phase at 600 °C. Additionally, in the case of increasing the temperature to 700 °C, the sample exhibits the rutile phase. Notably, no other phase was observed in XRD, indicating that the nitrogen element was highly dispersed in the $TiO_2$ crystal. It implies that no novel crystalline phase is formed [10].

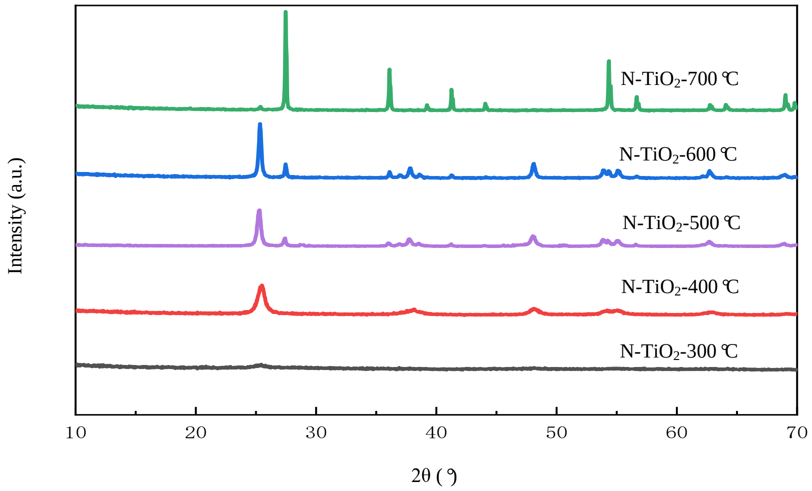


Figure 2: XRD Profiles of the N-$TiO_2$ Samples.

### 3.3. Analysis of Photocatalytic Properties

Figures 3 and 4 demonstrate the degradation effects of normal $TiO_2$ and N-doped $TiO_2$ on methyl orange solution under visible light irradiation at diverse annealing temperatures. From Figure 4, it can be seen that the catalytic effect of normal $TiO_2$ exhibits a trend of first decreasing and then increasing within 40 min at the annealing temperature of 300 °C to 700 °C. Notably, its degradation rate was 88.0% at 300 °C. As the temperature rose to 500°C, its degradation rate decreased to 35.2%. When the temperature continued to rise to 600 °C, however, its degradation rate increased significantly to 96.7%, indicating the optimal catalytic effect within this temperature range. Nevertheless, when the temperature was further raised to 700 °C, its degradation rate dropped back to 81.9%.

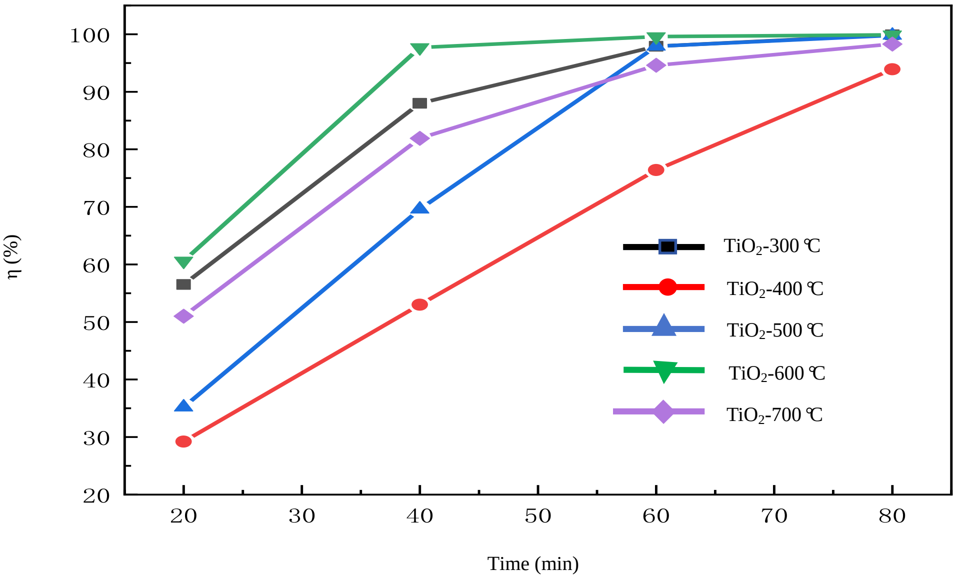


Figure 3: Degradation Rate of Methyl Orange Solution by $TiO_2$ at Various Annealing Temperatures.

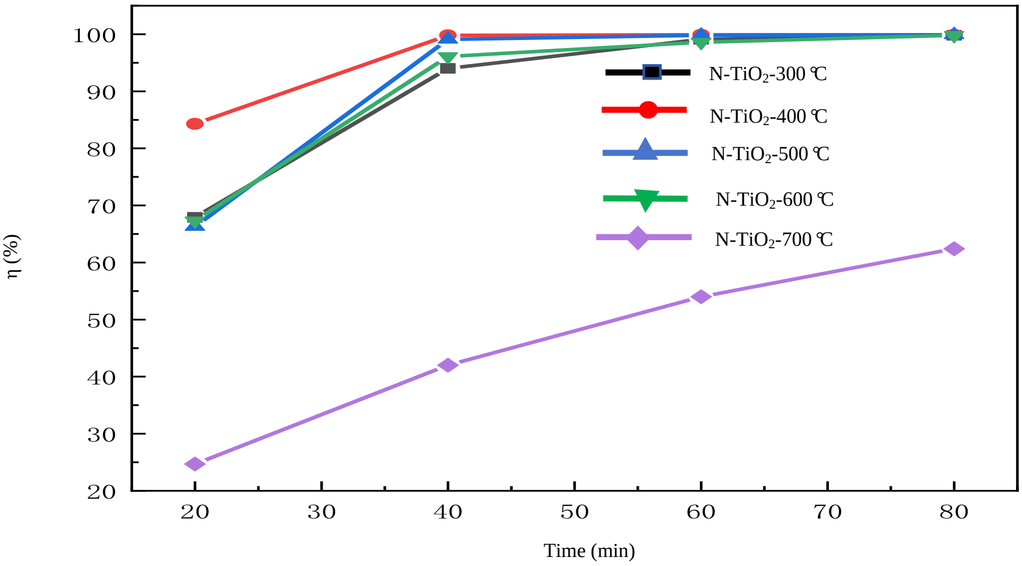


Figure 4: Degradation Rate of Methyl Orange Solution by N-doped $TiO_2$ at Various Annealing Temperatures.

The decrease in band gap width of N-doped $TiO_2$ implies that the material requires less photon energy, thus enabling it to absorb visible light with lower energy [11,12]. Conceptually, the band gap is defined as the energy difference between the valence band and conduction band, which determines the absorption and emission characteristics of materials for light. For $TiO_2$-based catalytic materials, a smaller band gap width means the utilization of a wider spectral range, thus improving the utilization of light energy. Under the irradiation of visible light, N-doped $TiO_2$ exhibited remarkable catalytic activity within 20 minutes. Moreover, most N-doped samples basically completed the degradation of methyl orange within 40 minutes. Particularly at the annealing temperature of 400 °C, its catalytic efficiency was as high as 99.9%, demonstrating excellent visible photocatalytic performance. When the annealing temperature was raised to 700 °C, however, the catalytic effect of N-doped $TiO_2$ decreased. Annealing temperature exerts a certain influence on the catalytic effect of normal $TiO_2$ and N-doped $TiO_2$. More exactly, normal $TiO_2$ at the high temperature of 600 °C showed the optimal catalytic effect. In contrast, N-doped $TiO_2$ exhibited extremely high catalytic activity at a lower annealing temperature, such as 400 °C. The preceding findings are beneficial to the optimization of the preparation process of $TiO_2$ [11,12]. Concurrently, while reducing the energy loss, this finding is helpful in achieving an efficient catalytic effect.

## 4. Conclusions

To sum up, this research prepares the samples of $TiO_2$ and N-doped $TiO_2$ by sol-gel method. Structural analysis indicates that the doping of nitrogen can improve the purity of anatase $TiO_2$. Furthermore, the catalytic degradation experiment demonstrates that the doping of nitrogen significantly improves the photocatalytic activity of $TiO_2$ in degrading methyl orange dye pollutants. Through changing the annealing temperature during the preparation process, this research implements annealing at 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C, respectively, to explore the effects of different annealing temperatures on doping properties. Test results reveal that N-doped $TiO_2$ samples annealed at 400 °C exhibit the optimal photocatalytic performance.

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