

Effect of Nitrogen-doping on photocatalytic activity of nanosized TiO₂ catalyst

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Abstract: Nitrogen-doped titania (TiO₂) photocatalyst were prepared by a simple sol-gel method using tetrabutyl titanate and triethylamine as precursors. The photocatalytic decomposition of methyl orange (MO) solution was used as a probe reaction to estimate the photocatalytic activity under ultraviolet and simulated visible light irradiation. The physical and photophysical properties of the photocatalyst were characterized by XRD, UV-Vis DRS and XPS. The results indicate that the simulated visible light photocatalytic ability of catalysts is improved, especially the nitrogen-doped sample calcined at 500°C (N500) showed excellent photocatalytic activity for methyl orange (MO) degradation under simulated visible light irradiation, which could be attributed to the nitrogen doping.

1. Introduction

As a safe, good biochemical stability, special photocatalytic properties materials, TiO₂ are widely used to deal with environmental pollution, water purification, wastewater treatment, hazardous waste control, and air purification. Because of the wide band gap (3.2eV), TiO₂ merely absorb less than 387nm ultraviolet light. It is great interest to enhance the absorption in the visible spectral range. Recently, many scientists have reported that non-metal atoms doping such as carbon, sulfur, and nitrogen in TiO₂ lattice is the most commonly used for decreasing the band gap. It is easy to intrude the nonmetal-atoms into crystal lattice of titanium oxide because the dimension of the atoms match with oxygen atom [1]. Nitrogen element doping can realize TiO₂ visible-light response and does not reduce the catalysis of ultraviolet light. Different physical and chemical methods have been introduced to synthesize nitrogen-doped titania, such as hydrothermal synthesis, sol-gel, magnetron sputtering, high-speed milling machine-chemical method, high-temperature calcination and oxidation of TiN. Wu [2] prepared visible-light-responsive nitrogen doped TiO₂ hollow spheres by acid-catalyzed hydrolysis. Suda [3] and Mwabora [4] used pulsed laser deposition and magnetron sputtering to fabricate nitrogen-doped TiO₂ thin films, respectively. Jung [5] synthesized nitrogen doped TiO₂ spheres with a mesoporous structure by hydrothermal process. However, these methods have the disadvantages of high equipment cost and complicated operation.

In our study, nitrogen doped nano TiO₂ photocatalyst were obtained by a sol-gel method, which was low energy consumption and easy to implement. The as-prepared samples were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), diffuse reflectance spectroscopy (DRS), and X-ray photoelectron spectroscopy (XPS). The effect of calcination temperature on the photocatalytic performance of TiO₂ was discussed.

2. Experiment

2.1 Preparation of samples

40 mL of anhydrous ethanol and 17 mL of butyl titanate were mixed into solution A. 40 mL of absolute ethanol was thoroughly mixed with 9 mL of double distilled water, A certain amount of glacial acetic acid and triethylamine were rapidly added dropwise and stirred until completely mixed as solution B. The solution A was then added dropwise with stirring to the solution B, continued to stir after mixing 30min, followed by aging in a closed beaker. After four days aging, the sol was aged in the oven at 80 °C for 10h, then placed in a muffle furnace, calcined at 400, 500, 550 and 600°C for 2h, labeled as N400, N500, N550, N600. For the purpose of comparison, the sample without the addition of triethylamine was also prepared and calcined at 500°C, labeled as pure.

2.2 Characterization of the sample

X-ray photoelectron spectrometer (ESCALAB250) produced by Thermo-VG Scientific in the United Kingdom was used for XPS analysis. The X-ray photoelectron spectroscopy was used to determine the crystalline phase of the samples. The samples were analyzed by D / Max-III A X-ray diffractometer. UV-Vis DRS was performed on a Shimadzu UV-3150 UV-Vis spectrophotometer.

2.3 Photocatalytic decomposition of methyl orange

The photocatalytic experiment was carried out with methyl orange as the model pollutant in SGY-1 photocatalytic reactor. The 300W high pressure mercury lamp with the main wavelength of 365nm and the 250W xenon lamp with the same composition of sunlight are used for the ultraviolet and visible light sources respectively. 250 ml of methyl orange solution containing an appropriate amount of TiO₂ samples was magnetically stirred, and air was aerated to the solution at a rate of 200 ml/min. 10ml of methyl orange solution was withdrawn and centrifuged every five or ten minutes. The supernatant was collected and the absorbance was measured at 464 nm to measure the degradation rate of methyl orange.

3. Results and discussion

3.1 XRD analysis of samples

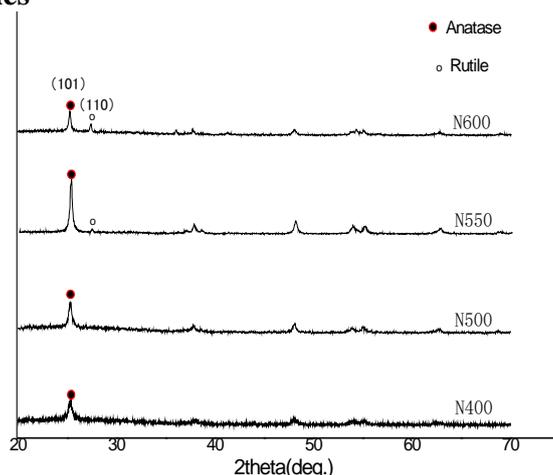


Fig.1 XRD patterns of N-TiO₂ samples calcined at different temperatures

Fig.1 shows the XRD patterns of the samples calcined at different firing temperatures. With increasing calcination temperature, the broad anatase diffraction peak narrowed gradually, and its intensity became stronger. The average particle size of N400, N500, N550 and N600 obtained using the Scherrer formula was 21.97, 23.05, 29.29 and 33.49nm respectively. We note that, With the rise of calcination temperature (from 400 to 600°C), the crystal form transferred gradually from anatase to rutile, and the crystal size grew gradually, the critical temperature was between 500 and 550°C.

N-TiO₂ powder did not show any Ti-N diffraction patterns with characteristics of crystalline phases mainly because the low content of nitrogen cannot be detected, or nitrogen has been incorporated into the crystal lattice of TiO₂ [6-7] .

3.2 UV- visible diffuse reflectance spectroscopy

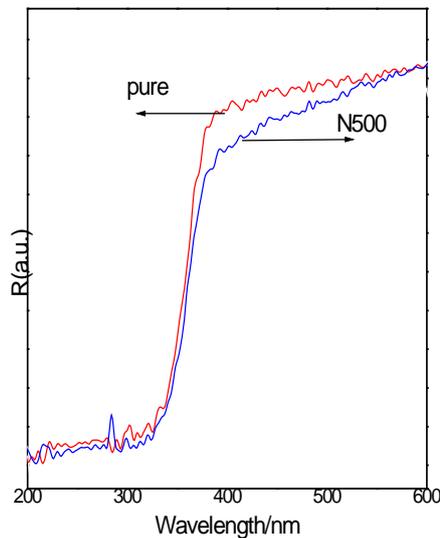


Fig.2 UV-Vis diffuse reflectance spectra of pure and N500

Fig.2 shows the UV-vis diffuse reflectance spectra over the wavelength range of 300–700 nm for N500 and pure. N500 exhibits stronger absorbance intensity in the UV light region compared to pure. It can be concluded that N doping improves the uv absorption ability. N500 shows a reflection platform at about 400nm, which is the sample of the intrinsic absorption limit, and this is correspond to the wide band gap (3.0 ~ 3.2 eV) of TiO₂. This visible light absorption is related to a certain number of oxygen vacancies and interstitial atoms produced during the preparation of TiO₂, which results in the generation of a certain number of defect energy levels in the forbidden band and the electronic transition [6]. At the same time, N500 nanocrystals absorb well into the visible region up to 550 nm and shows remarkable red shift to visible wavelength region and stronger absorption in the visible light as compared to pure . Therefore, it is understandable that in comparison with pure, N500 shows stronger absorption capacity under ultraviolet as well as visible light irradiation.

3.3 XPS

Fig.3 shows the XPS high-resolution scanning of N_{1s} samples calcined at 500 °C. The XPS peaks of N_{1s} appears at binding energy 399.7eV. This result is consistent with Hu [7] and Sato [8] et al. The peak at about 399.5 eV (398.4 EV-399.7 eV) was frequently observed for N-doped TiO₂ materials [9] . This binding energy is corresponding to the interstitial doped N_{1s} electron binding energy of the N atom, and the N atoms capture electrons from Ti and O, with electron density decreasing, such that interstitial N-doped atom are easily formed in the crystalline lattice [10] .

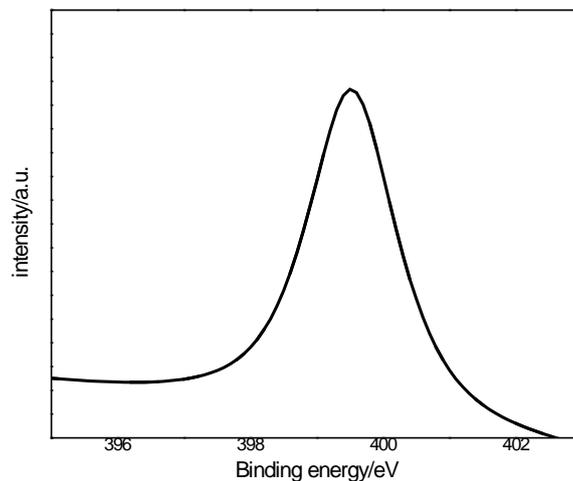


Fig.3 High resolution XPS spectra of N_{1s} taken on the surfaces of N500

3.4 Photocatalytic activity

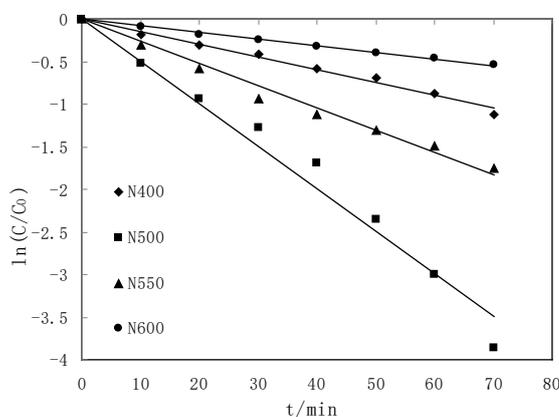


Fig.4 Dynamics curves of MO degradation under simulated sunlight for different photocatalysts

Fig.4 presents the photocatalytic activities of N-doped TiO₂ calcined at different firing temperatures. The photodegradation of methyl orange exhibits fairly good linear relationships, indicating that all reactions follow the first-order kinetics, and the apparent rate constants are listed in Table 1. The sample calcined at 500 °C exhibited a higher photocatalytic degradation rate. Obviously, the higher the temperature (from 500 to 600 °C) was, the lower the catalytic activity measured. It can be explained by the facts that activity of photocatalysts is largely affected by the crystallite size and surface state. The XRD results showed that with the rise of calcination temperature the proportion of the rutile phase and the crystal size grew, leading to a decrease in the photocatalytic activity of TiO₂. On the other hand, a proper amount of N doping can enhance the absorption of visible light [11-12]. With the increase of temperature, non-metallic nitrogen element is easy to be lost. At lower temperature, excess N doping leads to the formation of electron hole [13], the carrier recombination rate is accelerated and the photocatalytic activity is inhibited. In this experiment, the optimum temperature was 500 °C.

Table 1 First-order kinetics rate constants and relative coefficients for photocatalytic decomposition of MO on N-doped TiO₂

samples	N400	N500	N550	N600
K·min ⁻¹	0.015	0.050	0.026	0.008
R ²	0.988	0.975	0.982	0.993

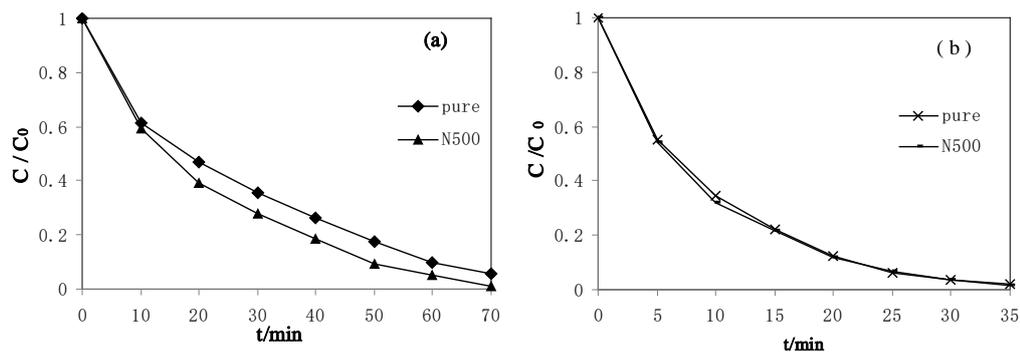


Fig.5 Photodegradation profiles of MO on pure and N500 under simulated sunlight(a) and ultraviolet(b)

The photocatalytic activities of pure and N500 on the degradation of methyl orange under simulated sunlight and UV light are shown in Fig.5. Compared with the pure TiO₂, N500 has better photocatalytic activity under UV light. In particular, the degradation rate of N500 is obviously higher than pure TiO₂ under simulated sunlight and the degradation of methyl orange within 50 min was 91.6 %.The high visible phototcatalytic activity of the sample is due to the nitrogen doping which is responsible for the red-shifted absorption edge of N500 as indicated by the DRS results in Fig.2.

4. Conclusion

N-TiO₂ were prepared by a sol-gel method using triethylamine as nitrogen raw material. It was found that calcination temperature has remarkable effects on the structure and activity of the catalysts, and the optimum temperature was 500 °C .The nitrogen-doped sample calcined at 500°C(N500) has a stronger visible light absorption from 400nm to 550nm, and its UV activity was better than that of pure.

5. Acknowledgments

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6. References

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