Study on Process Performance of N-Doped Porous Titanium Dioxide

Chao Wei1,2,*, Zhongjin Peng3, Pengju Zhang3, Zhongjin Peng3, Jiaqi Duan3

1School of Chemical Engineering, China University of Mining and Technology, Xuzhou 221116, China
2College of Xuhai, China University of Mining and Technology, Xuzhou 221008, China
3School of Materials Science and Engineering, China University of Mining and Technology, Xuzhou 221116, China

*Corresponding author e-mail: weichaoxh@163.com

Abstract. The template-free self-assembly method was used to prepare N-doped porous titanium dioxide. The structure and properties of the samples were characterized by XRD, TEM, fluorescence spectroscopy, Fourier Transform Infrared (FTIR) spectrum and degradation methyl of orange experiments. The results show that the porous titanium dioxide doped with N can promote the crystallization of titanium glycol at 175 °C and inhibit the crystallization at 185 °C. N-doped porous titanium dioxide can destroy the original Ti-O-Ti bond in ethylene glycol titanium and replace the vacancy left by a small part of oxygen from the original position, so as to improve the photocatalytic performance; and the photocatalytic ability of N-doped porous titanium dioxide of 3% with UV light is best and the photocatalytic ability of porous titanium dioxide with visible light is best when doping amount of N is 0.25%, which is much better than that of P25. However, the N-doped porous titanium dioxide can only be replaced by sub-bandgap energy with smaller visible energy Excitation, which also gives it limited ability to visible light catalysis.

1. Introduction
With the excessive utilization of resources and the serious pollution of nature, the ecological environment has suffered serious damage [1]. There is an urgent need to develop new functional materials that can use energy economically and efficiently without polluting the environment. Titanium dioxide has been widely used in industries such as dyes, sunscreen, toothpaste and ointment additives in the early 20th century [2-4]. But titanium dioxide only reacts in the ultraviolet region [5-7]. So, the realization of the response in the visible region has become a research hotspot. Through ion doping modification of TiO2, it can effectively inhibit the combination of electron and hole, and improve the photocatalytic activity. Meanwhile, doped ions can also reduce the band width of TiO2, thus realizing its light response in the visible region [8-12]. In this paper, a template-free self-assembly method was used to prepare N-doped porous titanium dioxide and improve the photocatalytic properties.
2. Preparation of N-doped porous titanium dioxide

The template-free self-assembly method was used to prepare doped N-porous titanium dioxide. In the first place, tetra-butyl titanate, ethylene glycol and ammonium chloride were mixed in a certain proportion. Preparation of ethylene glycol under 175 °C for 4 h and then the crystalline porous titanium dioxide is obtained through under 400w ultraviolet light irradiation for 2 and then calcinating at 400°C for 2 h. The experimental process is shown in figure 1. The doping amount of N (molar ratio of N/ (N+Ti) ) is 0.25%, 0.5%, 1%, 3% and 5% respectively.

![Figure 1. Flowchart of preparation of N-doped porous titanium dioxide.](image)

3. Results and Analysis

The structure and properties of the samples were characterized by XRD, TEM, fluorescence spectroscopy, Fourier Transform Infrared (FTIR) spectrum and degradation methyl of orange experiments.

3.1. XRD

Figure 2 shows that the synthesis temperature was at 175 °C, and the XRD spectrum of ethylene glycol titanium obtained under the different doping amount (0%, 0.25%, 0.5%, 1%, 3% and5%) of N. The figure shows that there is no strong absorption peak in the XRD of the un-doped ethylene glycol glycol titanium, and only a slight steamed bread peak appears, indicating that the un-doped ethylene glycol is amorphous. When the amount of mineral N is 0.25%, the characteristic peak of ethylene glycol titanium began, and with the improvement of N content, the characteristic peak of ethylene glycol titanium is more and more strong. When the amount of mineral N is 1%, the absorption peak is highest and then began to decline. It can be seen that doped N promote the crystallization of the glycol titanium, but when excessive amounts of doping destroys glycol titanium crystal structure, characteristic absorption peak.
Figure 2. XRD patterns of the as-prepared composite samples

Figure 3. XRD spectrum of pure and 3% N-doped of ethylene glycol titanium when synthetic temperature was 185°C
Figure 4. XRD spectrum of 3% N/ TiO2 when the synthetic temperature of ethylene glycol titanium was 175°C and 185°C

Figure 3 is the XRD spectrum of ethylene glycol titanium in different N-doped under temperature 185°C. The figure shows that the un-doped glycol titanium has a strong absorption peak. When the amount of mineral N is 3%, the absorption peak disappears and no steamed bread peak, indicating that the glycol titanium mixing N become disordered phase, and the effect of doping N element on crystal structure is different under different temperature.

Fig 4 is the XRD spectrum of 3% N-doped TiO₂ when the synthetic temperature of ethylene glycol titanium was 175°C and 185°C. By comparing with the PDF card, it is concluded that the synthetic product is the anatase-TiO₂ and there is no new absorption peak, which indicates that there is no new material produced after doping N.

3.2. FTIR

Figure 5. Infrared spectrum of pure and 3% N-doped of ethylene glycol titanium when synthetic temperature of ethylene glycol titanium was 175 °C
Figure 5 shows that the absorption peak of 633 cm\(^{-1}\) and 595 cm\(^{-1}\) is the Ti-O bond in ethylene glycol titanium, and the absorption peak of 116 cm\(^{-1}\) and 1060 cm\(^{-1}\) corresponds to C-C-O stretching vibration in ethylene glycol, and the absorption peak of 537 cm\(^{-1}\), 498 cm\(^{-1}\) and 443 cm\(^{-1}\) corresponds to the stretching and bending vibration of Ti-O-Ti. The preparation of the material is the composition of ethylene glycol titanium.

The infrared spectrogram of the 3% N-doped ethylene glycol titanium showed that the telescopic bending vibration peak of the Ti-O-Ti was disappeared in the range of 400cm\(^{-1}\) to 300cm\(^{-1}\), which indicates that Ti-O-Ti are destroyed, N ions have the tendency to replace the oxygen ions. Because of the less amount of mineral N, only a small amount of oxygen was replaced so there is no obvious absorption peak on the infrared spectrogram.

3.3. Fluorescence Spectroscopy

Fluorescence spectra is derived from carrier recombination. Therefore, the fluorescence spectrum can reveal the carrier capture, transfer and separation efficiency, so as to determine the semiconductor light in the life of electrons and holes.

Figure 6 is the fluorescence spectrum of P25, pure TiO2 and 0.25 % N-doped when the synthesis temperature is 175°C and 185°C. According to the above figure, three different excitation emission peaks appear at the excitation wavelength of 390nm, 410nm and 490nm, respectively corresponding to the semiconductor band gap width at 3.18, 3.04 and 2.53ev emission peaks respectively. The fluorescence peak of 410nm and 490nm is derived from the free carrier band transition. The fluorescence intensity of 0.25 % N-doped porous titanium dioxide is lower than pure TiO2 and P25 when the synthesis temperature is 175°C. This indicates that the suitable synthesis temperature and appropriate nitrogen ion content can greatly reduce the compound rate of electron and hole carrier of porous titanium dioxide.

![Fluorescence spectra of P25 and different N-doped TiO2](image)

**Figure 6.** Fluorescence spectra of P25 and different N-doped TiO2

3.4. TEM

Figure 7 shows that the un-doped porous titanium dioxide nano-level micro-pores are relatively flat and have a certain accumulation rule, which is not haphazard accumulation, but an orderly growth. However, the nanoparticles with N are smaller than those without nitrogen, so they are higher than the surface area, and the photocatalytic efficiency is better.
3.5. Photocatalytic Performance under Ultraviolet Light

Figure 8 shows that the catalytic performance of N-doped titanium dioxide has been improved. When the amount of mineral N is 3%, the photocatalytic performance is the best. Compare with the pure TiO2, the amount of mineral N is 3% has obvious improvement, and its performance is the best, and there is a small gap with P25.

N atom replaces oxygen vacancy position. Along with the increase of doping amount, the oxygen vacancy position more, and the gap could prompt recombination of hole and electron, so in a certain range will exists an optimal value.

The addition of nitrogen caused the lattice distortion of porous titanium dioxide, and the appropriate lattice distortion generates more oxygen vacancies, so in the bottom of the conduction band can introduce more shallow level as capture electron trap and promote the separation of electrons and holes.

Figure 8. Methyl orange degradation curve of TiO2 with different N doping when synthetic temperature of ethylene glycol titanium was 175 °C.
3.6. Photocatalytic Performance under Visible Light

![Photocatalytic Performance under Visible Light](image)

**Figure 9.** The degradation curve of methyl orange under visible light of TiO$_2$ with different N doping when synthetic temperature of ethylene glycol titanium was 175 °C

Figure 9 shows that the photocatalytic capacity of N-doped titanium dioxide in visible light is also present, and the catalytic ability is better than that of pure TiO$_2$. When the proportion of N is 0.25%, the photocatalytic capacity of N-doped titanium dioxide has the strongest catalytic performance under visible light and is superior to P25. As a result of nitrogen to replace the position of the parts of the porous titanium dioxide lattice oxygen, above the valence band formed a single narrow N2P band and the narrow band responds to the sensitization of visible light. UV light can excite electrons in the valence band and the independent narrow band, and visible light can not excite electrons in the valence band, so the photocatalytic capability of visible light is inferior to that of ultraviolet photocatalysis. As the vacancy position of oxygen increases with the increase proportion of N, the oxygen vacancy position promotes the recombination of hole and electron. With the decrease of quantum yield, the activity of visible light decreased with the increase of N. Although N can make porous titanium dioxide in visible light has a certain catalytic ability but it can only change the properties of near the valence band or very close to the conduction band to keep it in a defective energy state, and the TiO$_2$ only has an effect on the position of the sub-band gap (hv2 and hv3) with low energy in the visible region.

4. Conclusion

Doped nitrogen can promote glycol titanium crystal under 175 °C and inhibit the crystallization under 185 °C, but it doesn't change the structure of titanium dioxide. The addition of N can destroy the Ti-O-Ti bond in the ethylene glycol titanium and replace a small fraction of the oxygen left vacant, thus enhancing the photocatalytic performance. The photocatalytic performance of porous titanium dioxide doped with 3% N was optimized. Doped nitrogen improve the visible light catalytic ability of porous TiO$_2$, and when the optimal doping amount is 0.25%, the visible light catalytic ability of porous TiO$_2$ far more than P25, but adding nitrogen of porous titanium dioxide can be excited by sub-band gaps with low energy in the visible region and limited the ability to catalyze visible light.

**Acknowledgments**

This work is supported by Jiangsu University of natural science research project (No.15KJD430003).
References

[1] Fujishima A. Photoelectrochemistry and Photocatalysis Will Help Us Realize a Green, Sustainable Future [J]. Electrochemistry, 2011, 79 (10): 759-759.

[2] Han Z, Zhang J, Yang X, et al. Synthesis and Photoelectric Property of Poly (3-Octylthiophene)/Titanium Dioxide Hybrid[J]. Journal of Inorganic and Organometallic Polymers and Materials, 2009, 20 (1): 32-37.

[3] Hashimoto K, Irie H, Fujishima A. TiO₂ Photocatalysis: A Historical Overview and Future Prospects [J]. Japanese Journal of Applied Physics, 2005, 44 (12): 8269-8285.

[4] Zhang K, Liu Q, Wang H, et al. TiO₂ Single Crystal with Four-Truncated-Bipyramid Morphology as an Efficient Photocatalyst for Hydrogen Production [J]. Small, 2013, 9 (14): 2452-2459.

[5] Wang J, Cao F, Bian Z, et al. Ultrafine single-crystal TiOF₂ nanocubes with mesoporous structure, high activity and durability in visible light driven photocatalysis [J]. Nanoscale, 2014, 6 (2): 897-902.

[6] Bian Z, Zhu J, Wang S, et al. Self-assembly of active Bi₂O₃/TiO₂ visible photocatalyst with ordered mesoporous structure and highly crystallized anatase [J]. Journal of Physical Chemistry C, 2008, 112 (16): 6258-6262.

[7] Liu G, Zhao Y, Sun C, et al. Synergistic effects of B/N doping on the visible-light photocatalytic activity of mesoporous TiO₂ [J]. Angewandte Chemie, 2008, 47 (24): 4516-4520.

[8] Crossland E J W, Noel N, Sivaram V, et al. Mesoporous TiO₂ single crystals delivering enhanced mobility and optoelectronic device performance [J]. Nature, 2013, 495 (7440): 215-219.

[9] Li H, Bian Z, Zhu J, et al. Mesoporous titania spheres with tunable chamber structure and enhanced photocatalytic activity [J]. Journal of the American Chemical Society, 2007, 129 (27): 8406-8407.

[10] Wang P, Yap P-S, Lim T-T. C-N-S tridoped TiO₂ for photocatalytic degradation of tetracycline under visible-light irradiation [J]. Applied Catalysis A: General, 2011, 399 (1-2): 252-261.

[11] Asahi R, Morikawa T, Ohwaki T, et al. Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides [J]. Science, 2001, 293 (5528): 269-271.

[12] Štengl V, Henych J, Vomáčka P, et al. Doping of TiO₂-GO and TiO₂-rGO with noble metals: synthesis, characterization and photocatalytic performance for azo dye discoloration [J]. Photochemistry and Photobiology, 2013, 89 (5): 1038-1046.