Ultrasonic Preparation of Nitrogen-doped TiO$_2$ Nanocrystalline Photo Catalysts and Evaluation of Photocatalytic Activity

Huifang Zhang$^{1,2,*}$, Zixin Lu$^1$, Mengyao Tang$^1$, Wenping Cao$^1$, Kangni Cai$^1$ and Hanhu Liu$^2$

$^1$College of Environmental Engineering, Xuzhou Institute of Technology, Xuzhou 221000, China; $^2$School of Environmental Science and Spatial Informatics, China University of Mining and Technology, Xuzhou 221000, China.

*Corresponding author e-mail: kdzh82@163.com

**Abstract.** Pure TiO$_2$ and N-doped nano-TiO$_2$ photo catalysts were individually prepared following the sol-gel method under ultrasonic conditions. The photocatalytic decomposition of methyl orange (MO) solution under ultraviolet and visible light irradiation was used as a probe reaction to estimate their photocatalytic activities. The particle size, crystal structure, and optical properties of the prepared TiO$_2$ were performed by X-ray diffraction, transmission electron microscopy and UV–vis diffuse reflectance spectroscopy. The results suggest that ultrasound significantly reduced the size of the TiO$_2$ particles, improved particle dispersion, which in turn improved the photocatalytic activity of TiO$_2$ under ultraviolet light. Ultrasound also promoted the doping of non-metal nitrogen and markedly enhanced the visible light absorption capacity of the N-doped nano-TiO$_2$. Compared with pure TiO$_2$, the degradation rate for MO under visible light of U-N-TiO$_2$ was increased by 70%.

**Keywords.** Ultrasound; titanium dioxide; nitrogen doping; photocatalytic oxidation; methyl orange; degradation.

1. Introduction

Nano-TiO$_2$ is a safe and biochemically stable material with special photocatalytic properties, widely used in the chemical industry and environmental protection [1-2]. It does, however, also have limitations: namely, the spectral response range is narrow and requires excitation by ultraviolet light to produce electron-hole pairs. These photo-generated electron–hole pairs are prone to recombination. In addition, the catalytic efficiency of the TiO$_2$ photo catalyst is still quite low, requiring further improvement. Results herein show that doping of TiO$_2$ with non-metal N can narrow the band-gap of TiO$_2$ and effectively expand the spectral response range of TiO$_2$, which improves its absorption capacity of visible light [3-6]. Ultrasound reactions are generally carried out at ambient temperature and pressure, and are currently under focus for the preparation of optical, magnetic, and catalytic nanomaterials. These special physical and chemical conditions accelerate the hydrolysis reaction,
decrease the grain and particle size of TiO2, improve its dispersion, and increase its surface area [7, 8]. Theoretically, the acoustic cavitation can promote incorporation of the doping component into TiO2 [9, 10].

In this work, ultrasound was applied to the preparation of pure nano-TiO2 and non-metal N-doped TiO2 by the sol-gel method in order to promote the crystallization of TiO2. This was seen to improve the effect of non-metal N-doping and broaden the spectral response range of TiO2. Characterizations of the prepared catalysts were conducted to investigate the physical chemistry and optical properties. At the same time, the photo catalytic degradation of methyl orange by modified TiO2 was investigated.

2. Experiments

2.1. Preparation of N-doped TiO2
17 ml tetra butyl titan ate (Ti(OC4H9)4, TBOT) was mixed with 40 ml anhydrous ethanol, and then added drop wise to a mixture containing acetic acid, deionized water, and ethyl alcohol. Then, 0.7 ml triethylamine was added drop wise as the nitrogen source. This mixture was solicited under vigorous mechanical stirring and high intensity ultra-sonication of 28 kHz. The final mixture formed a uniform, transparent sol-gel, followed by aging in a closed beaker. The mixture was dried at 80 °C for 10 h, calcined at 500 °C for 2 h, and grinded to obtain N-doped TiO2 powder, denoted as U-N-TiO2. N-doped TiO2 that was prepared without ultrasonic treatment is denoted as N-TiO2. The un-doped pure TiO2 powder prepared under ultrasonic conditions is denoted as U-TiO2, and pure TiO2 powder without ultrasonic treatment is denoted as pure TiO2.

2.2. Characterization
The morphology of aggregated particles and crystallite size were obtained via TEM imaging with applied scan accelerating voltage and magnification of 100 kV and 135,000 times, respectively. The X-ray photoelectron spectroscopy was used to determine the crystalline phase of the samples. The samples were analyzed by D / Max-IIIA X-ray diffract meter. UV-Vis DRS was performed on a Shimadzu UV-3150 UV-Vis spectrophotometer.

2.3. Photo catalytic Degradation Experiment
Photo catalytic activity of the prepared samples was first evaluated using methyl orange as the probe. The photo catalytic degradation experiments were conducted in a multi-function photochemical reactor, using high-pressure mercury and xenon lamps to generate ultraviolet and visible light irradiation, respectively. The photo catalysts (0.20 g under UV light and 0.25 g under visible light) were added to 250 mL of methyl orange solution with a concentration of 20 mg/L and the suspension was ultrasonically dispersed for 15 min. The resulting mixture was then stirred using a magnetic stirrer and fed O2 at a flow rate of 200 mL/min for 15 min under dark conditions, in order to equilibrate the adsorption and desorption of the dye on the surface of TiO2. The light source was turned on and the timer was started when the source became stable. The samples were collected after regular time intervals, and absorption at 464 nm was obtained on a UV-vis spectrophotometer and the changes in MO concentration were tracked.
3. Results and Discussion

3.1. Analysis of crystal form and morphology of TiO2

Figure 1. XRD patterns of pure TiO2 (top) and U-TiO2 (bottom)

The XRD patterns of pure TiO2 and U-TiO2 are shown in Fig. 1. It can be seen in Fig. 1 that the diffraction peak in the anatase phase (101 plane, $2\theta = 25.3^\circ$) of U-TiO2 is much sharper than that of pure TiO2, indicating that the anatase structure of U-TiO2 is more regular and has higher crystallinity. The average particle size of U-TiO2 calculated using the Scherrer formula was approximately 15 nm, whereas that for pure TiO2 was about 20 nm.

Figure 2. TEM images of (a) pure TiO2 and (b) U-TiO2

TEM images of pure TiO2 and U-TiO2 are shown in Fig. 2. These images show severe agglomeration between pure TiO2 particles. In comparison, the particle size distribution range of U-TiO2 is narrower, the particle contours are clearer, and the dispensability is better than that of pure TiO2. Fig. 2b does, however, show some crystal aggregation. During sol-gel preparation of nano-TiO2, colloidal particles have large specific surface energies, and are thus thermodynamically unstable. As a result, the particles have a tendency to aggregate, but ultrasonic cavitation can produce a large number of tiny bubbles on the surface of solid particles that greatly reduce the specific surface free energies of small grains and inhibit the aggregation and growth of grains [11]. In addition, ultrasonic cavitation generated by high-pressure shock waves and micro-jets also play a role in the crushing effect, thereby promoting the hydrolysis of the titanium organic ester salt, and resulting in better granulation of the TiO2 gel.
3.2. **UV-Visible Diffuse Reflectance Spectral Analysis of Samples**

![Figure 3](image)

**Figure 3.** The UV-Visible diffuse reflectance spectra of the samples

The ability of TiO2 to absorb light usually changes after nonmetal doping [12]. The UV-visible diffuse reflectance spectra of pure TiO2, N-TiO2 and U-N-TiO2 are shown in Fig. 3. It can be seen that N-doping significantly affects the light absorption characteristics for the TiO2 catalysts. At about 400 nm, pure TiO2 exhibits a reflection platform, while N-TiO2 and U-N-TiO2 both show tailing phenomenon as the optical absorption edge shifted to a longer wavelength direction, exhibiting a “red shift” at the absorption edge. This is because of the nitrogen in the N-TiO2 catalyst partially replacing oxygen, where the replacement of the 2p band of oxygen with the 2p band of nitrogen results in a narrowing of the band-gap[4,13], and a broadening of the response wavelength to the visible region. On the other hand, the absorption intensity of visible light is higher than that for N-TiO2. This is probably because ultrasound can cause sol-gel to react more effectively with triethylamine, thus allowing more N incorporation into the TiO2 catalyst. This further goes to prove that on the basis of N doping, the application of ultrasound can be effective for improving the photo catalytic activity of TiO2 under visible light.

3.3. **Evaluation of photocatalytic activity of the samples**

![Figure 4](image)

**Figure 4.** Kinetic curves of photocatalytic degradation of methyl orange by pure TiO2 and U-TiO2 under UV irradiation

- ● Pure TiO2
- ■ U-TiO2
The kinetic curves for photo catalytic degradation of methyl orange by pure TiO2 and U-TiO2 under UV irradiation are shown in Fig. 4. Fig. 4 shows that the photo catalytic degradation rate of TiO2 prepared under ultrasonic condition was markedly enhanced from pure TiO2. The first order reaction kinetic constants for TiO2 and U-TiO2 were 0.1142 min\(^{-1}\) and 0.1310 min\(^{-1}\), respectively. The larger the kinetic constant of a first order photo catalytic degradation, the stronger the photo catalytic activity of the catalyst. Ultrasonic treatment of catalyst was found to increase the photo catalytic degradation rate of TiO2 under ultraviolet light by 15%. The activity of the semiconductor photo catalyst has been shown to be influenced by crystallite size, specific surface area and surface morphology, with the time of electron or hole reaching the surface proportional to the square of the particle radius [14]. Therefore, the smaller the TiO2 particle, the shorter the time taken by the carrier to reach the surface, the smaller the electron-hole recombination probability. This results in a greater probability of surface absorption by the reactant, and higher catalytic activity. The XRD results show that the average size of the particles prepared under ultrasonic conditions were smaller, and consequently had better dispensability.

The kinetic curves for photo catalytic degradation of methyl orange by pure TiO2 and U-TiO2 under visible light irradiation are shown in Fig. 5. It is shown once again that the photo catalytic degradation of methyl orange by pure TiO2, N-TiO2 and U-N-TiO2 are consistent with first-order kinetics. The first order reaction kinetic constants for TiO2, N-TiO2 and U-N-TiO2 were 0.0349, 0.0482 and 0.0593 min\(^{-1}\), respectively. Compared with pure TiO2, the rate of degradation using U-N-TiO2 and N-TiO2 was increased by 70% and 23%, respectively. The results show that ultrasound promotes more effective doping of non-metal N, and the activity of TiO2 under visible light was improved to some extent. These results were consistent with the results of the UV-visible diffuse reflectance spectra of the samples. The N-doping broadens the range of absorption spectra of TiO2 and enhances the utilization of visible light by TiO2.

4. Conclusion
By application of ultrasound to the preparation of TiO2 photo catalysts, the produced U-TiO2 nanoparticles had more regular anatine structure, higher crystallinity, and smaller particle size, while promoting the doping of non-metal N. Compared with pure TiO2 and N-TiO2, ultrasonic treatment increased the photo catalytic degradation rate of pure TiO2 under ultraviolet light by 15%, and increased the photo catalytic degradation rate of N-TiO2 under visible light by 23%.
Acknowledgments
The work was supported by grants from the Science and Technology Plan Projects of Ministry of Housing and Urban-Rural Development of the People’s Republic of China under Grant Nos. R22016061; the Young Project of Xuzhou Institute of Technology under Grant No. XKY2016231; and the Innovative Entrepreneurship Training Program for College Students under Grant No.XCX2017158.

References
[1] X.Chen, J.Zhang, Y. Huang, Catalytic reduction of nitric oxide with carbon monoxide on copper-cobalt oxides supported on nano-titanium dioxide. Environ Sci. 21(2009) 1296-1301.
[2] M. Hussain, R. Ceccarclli, D.L. Marchisio, D. Fino, N. Russo, Synthesis, characterization and photo-catalytic application of novel TiO2 nano-particles. Chem Eng J, 151(2010) 45-51.
[3] C.C.Hu, T.C.Hsu, S.-Y.Lu, Effect of nitrogen doping on the microstructure and visible light photocatalysis of titanate nanotubes by a facile cohydrothermal synthesis via urea treatment. Applied Surface Science 280 (2013) 171-178.
[4] R.Asahi, T.orikawa, T.Ohwaki, Visible-light photocatalysis in nitrogen-doped titanium oxides. Science 293 (2001)269-271.
[5] R.He, W.He, Ultrasound assisted synthesis of TiO2–reduced graphene oxide nanocomposites with superior photovoltaic and photocatalytic activities. Ceramics International, 42(2016)5766-5771.
[6] J.C.Yu, J.Yu, L.Zhang, W.Ho, Enhancing effects of water content and ultrasonic irradiation on the photocatalytic activity of nano-sized TiO2 powders[J]. J Photochem Photobiol, A, 148 (2002) 263-271.
[7] D.L. Li, J.Wang, X.Li, H.L. Liu, Effect of ultrasonic frequency on the structure and sonophotocatalytic property of CdS/TiO2 nanocomposite. Materials Science in Semiconductor Processing, 15(2012)152–158.
[8] S. Senthilkumaar, K. Porkodi, R.Vidyalakshmi, Photodegradation of a textile dye catalyzed by sol-gel derived nanocrystalline TiO2 via ultrasonic irradiation. J. Photochem. Photobiol. A 170(2005)225-232.
[9] J.Ouyang, M.Chang, Y. Zhang, X. Li, CdSe-sensitized TiO2 nanotube array film fabricated by ultrasonic-assisted electrochemical deposition and subsequently wrapped with TiO2 thin layer for the visible light photoelectrocatalysis. Thin Solid Films. 520(2012)2994-2999.
[10] Z.Liu, X. Quan, H. Fu, X. Li, K.Yang. Effect of embedded-silica on microstructure and photocatalytic activity of titania prepared by ultrasound-assisted hydrolysis [J]. Appl Catal,B, 2004(52):33-40.
[11] P.S.Awati, S.V.Awate, P.P.Shah, V.Ramaswamy, Photocatalytic decomposition of methylene blue using nanocrystalline anatase titania prepared by ultrasonic technique. Catal.Commun. 4 (2003) 393–400.
[12] J.Yu, G.Dai, Q.Xiang, Fabrication and enhanced visible-light photocatalytic activity of carbon self-doped TiO2 sheets with exposed 001 facets. J Mater Chem. 1 (2011) 1049–1057.
[13] G.Liu, Y.Zhao, C.Sun, F. Li, L. Max, H.Cheng, Synergistic effects of B/N doping on the visible-light photocatalytic activity of mesoporous TiO2. Angew. Chem. Int. Ed. 47(2008)4516–4520.
[14] S.Liu, H.Liu, Photocatalytic and Optoelectronic Catalytic Basis and Application, Chemical Industry Press, Beijing,2007,pp.156-159.