

# Photocatalytic decomposition of methylene orange using nitrogen-doped titania prepared by ultrasonic technique

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**Abstract.** Nitrogen-doped titania (TiO<sub>2</sub>) photocatalysts were prepared by sol-gel process coupled with ultrasonic irradiation at room temperature. 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 physico-chemical properties of the samples were investigated by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), diffuse reflectance spectroscopy (DRS), and X-ray photoelectron spectroscopy (XPS). A more uniform nanoparticle dispersion, marginally higher surface area, smaller grain size, and higher phase purity are some advantages of preparing TiO<sub>2</sub> by the ultrasonic technique. The nitrogen-doped titania prepared by ultrasonic technique were more effective than the samples prepared by conventional stirring method. Its UV-Vis diffuse reflectance spectra was red shifted compared to the un-doped sample and it showed high decomposition of MO under ultraviolet as well as visible light irradiation.

## 1. Introduction

Titania (TiO<sub>2</sub>) has been extensively used in air purification, wastewater treatment, and hazardous waste control because of its desirable properties, such as outstanding chemical stability, high photocatalytic activity, relatively low cost, and non-toxicity [1,2]. However, it can only be excited under ultraviolet light of less than 387 nm due to its very wide band gap (3.2 eV). Electron-hole recombination can also inhibit the photocatalytic reaction process. These issues restrict its practical application. It is therefore of great interest and importance to extend the absorption wavelength range of TiO<sub>2</sub> to the visible light region. Previous studies have found that nitrogen-doped TiO<sub>2</sub> (N-TiO<sub>2</sub>) has a higher visible photocatalytic activity since it can absorb visible light [3-5]. Different physical and chemical methods have been studied for the synthesis of N-TiO<sub>2</sub>, such as hydrothermal synthesis [6], ion exchange [7], ion implantation [8], sol-gel methods, magnetron sputtering, high-speed milling machine-chemical method, high-temperature calcination and oxidation of TiN, etc. [9,10]. However, most are very time-consuming and require specific pH control and high temperature or through complex multistep reaction processes. 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. Powerful ultrasound is used to stimulate chemical processes in liquids since it



causes novel chemical reactions and physical changes which would not otherwise occur. These special physical and chemical conditions accelerate the hydrolysis reaction, decrease the grain and particle size of  $\text{TiO}_2$ , improve its dispersion, and increase its surface area [11, 12]. The size and morphology of  $\text{TiO}_2$  nanocomposites are closely related to the ultrasonic frequency; the minimum size is obtained at low frequency (20 kHz) [13]. Moreover, acoustic cavitation can promote incorporation of the doping component into  $\text{TiO}_2$  [14].

Herein, we report a novel ultrasonic technique (at frequency 28 kHz) coupled with a simple sol-gel method for the synthesis of nitrogen-doped titania. On one hand, nitrogen doping enlarges the light absorption range of  $\text{TiO}_2$  to enhance its photocatalytic efficiency under visible light. On the other hand, ultrasonication can control the particle size and distribution of  $\text{TiO}_2$ .

## 2. Methods

### 2.1. Synthesis

Nitrogen-doped nanosized  $\text{TiO}_2$  was synthesized using tetra butyl titanate ( $\text{Ti}(\text{OC}_4\text{H}_9)_4$ , TBOT) in the presence of water and ethyl alcohol absolute under ultrasonic irradiation. 17 ml TBOT and 40 ml ethanol were mixed and then added drop wise to a mixture containing acetic acid, deionized water, and ethyl alcohol. This mixture was sonicated under vigorous mechanical stirring and high intensity ultrasonication of 28 kHz. Then, 0.7 ml triethylamine was added drop wise as the nitrogen source. The mixture was then irradiated in an ultrasonic cleaning tank (28 kHz) for 1 h, followed by aging in a closed beaker at room temperature for 4 d. The wet gel was then dried at 80 °C (353 K) for approximately 10 h, collected, and ground into a fine powder. The dried powder was finally calcined in a muffle furnace at 500 °C (773 K) for 2 h and labeled as UN- $\text{TiO}_2$ . The other nitrogen-doped  $\text{TiO}_2$  sample was prepared under conventional stirring method without ultrasonic irradiation, labeled as N- $\text{TiO}_2$ . As a reference, pure  $\text{TiO}_2$  was prepared using the same procedure except that without triethylamine doping or ultrasonic irradiation, labeled as O- $\text{TiO}_2$ .

### 2.2. Characterization

$\text{TiO}_2$  samples were characterized by XRD, TEM, XPS, and UV-vis DRS. The chemical composition of  $\text{TiO}_2$  dried powders were obtained using a D/Max-III diffract meter with an applied accelerating voltage of 40 kV and current of 30 mA. 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. XPS was used to identify the atom level doping of N in  $\text{TiO}_2$  samples with  $\text{AlK}\alpha$  radiation. All binding energies were referenced to the C1s peak at 284.6 eV of surface adventitious carbon. The diffuse reflectance spectra (200 to 700 nm) of  $\text{TiO}_2$  dry powders were obtained on an UV-vis spectrophotometer.

### 2.3. Photocatalytic decomposition of methyl orange (MO)

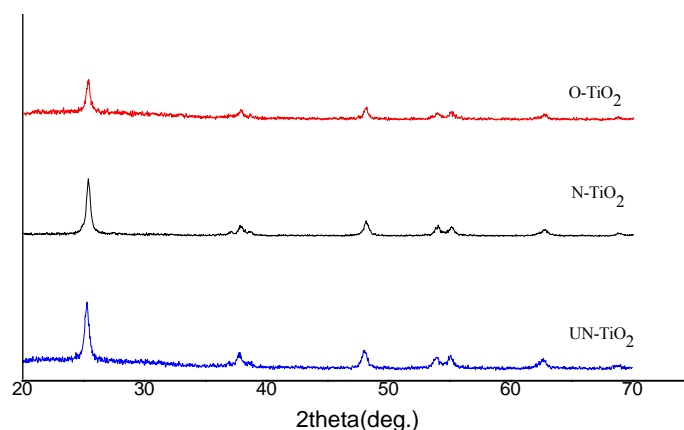
Photocatalytic experiments with MO solution were performed in a glass photocatalytic reactor. Irradiation was carried out using 365 nm UV and 250 W xenon lamps. MO solution (250 mL) was magnetically stirred and ultrasonically irradiated. Oxygen was continuously pumped into the reaction solution before and during illumination. Ten mL sample was taken every five or ten min and centrifuged (5000 rpm). 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. XRD analysis

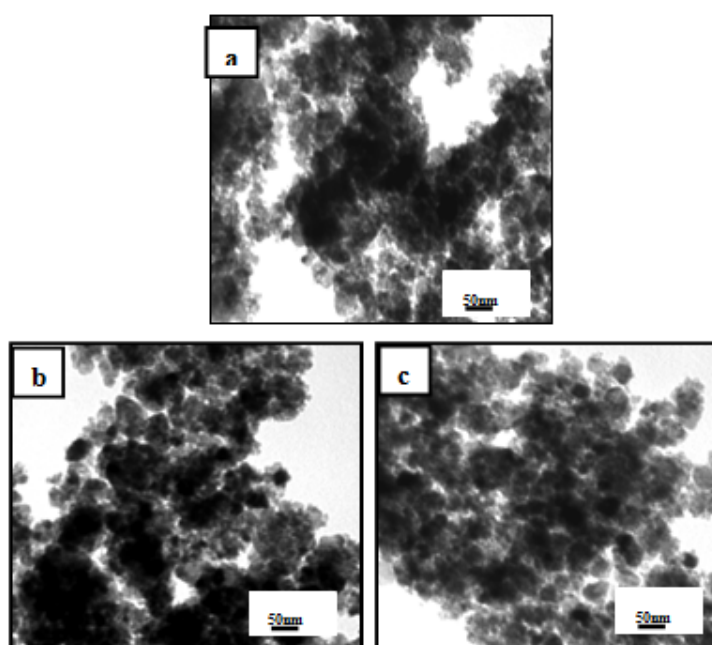
Fig. 1 shows the XRD patterns of the dry  $\text{TiO}_2$  powders. Identification of the  $\text{TiO}_2$  phase, confirmed by comparison with accepted standard peaks from JCPDS, revealed that the three kinds of powders contained only the anatase phase; no peaks corresponding to the rutile phase were observed. The full-

width at half-maximum of the UN-TiO<sub>2</sub> samples are broadened, which might be attributed to ultra sonication. The average particle size of UN-TiO<sub>2</sub>, N-TiO<sub>2</sub> and O-TiO<sub>2</sub> obtained using the Scherrer formula was 19.85, 22.85 and 22.18 nm, respectively. We note that samples prepared with ultra sonication have narrow particle size range compared to those prepared by conventional stirring methods. The apparent width and intensity of the (101) peak of N-TiO<sub>2</sub> are large. This can be explained by the ultrasonic cavitation process. The implosive collapse of bubbles in a liquid solution can produce extremely high temperatures during hydrolysis, which accelerated the hydrolysis reaction and promoted formation of the anatase phases [12].



**Figure 1.** XRD patterns of samples.

### 3.2. TEM images

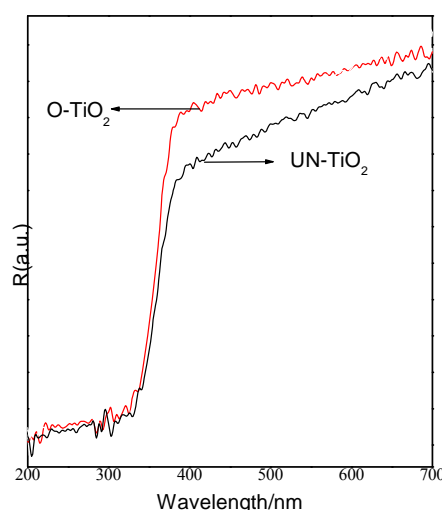


**Figure 2.** TEM photographs of samples.

In order to further elucidate the size and crystal structure of the nanocomposites, TEM micrographs of O-TiO<sub>2</sub>, N-TiO<sub>2</sub> and UN-TiO<sub>2</sub> were obtained, as shown in Fig.2. These three catalysts are all nanosized.

The size of the primary particle is  $20 \pm 2$  nm, which agrees with the values determined from XRD analyses. As shown in Fig. 2a and Fig. 2b, both O-TiO<sub>2</sub> and N-TiO<sub>2</sub> powder show a dense, aggregated structure, resulting in a decreased surface area. Fig. 2c shows that UN-TiO<sub>2</sub> contains more uniformly sized and less agglomerated particles compared to N-TiO<sub>2</sub>. The TEM and XRD data indicate that particles are likely to be nan agglomerates of 2-3 crystallites in the UN-TiO<sub>2</sub> sample and 5-6 crystallites in the N-TiO<sub>2</sub> sample, in which agglomeration is more pronounced. This clearly reveals the role of ultra sonication, which results in a less agglomerated and more homogeneous sample. It is well known that collapsing bubbles create extreme temperatures and pressures during aqueous sonochemical processes. Cavitation bubbles undergo oscillations and increase in size before finally collapsing, resulting in higher temperature and more turbulent flow conditions. Cavitation and shockwaves can accelerate solid particles to high velocities, and antiparticle collisions can disrupt surface adsorption between particles and reduce agglomeration [15].

### 3.3. UV-vis DRS



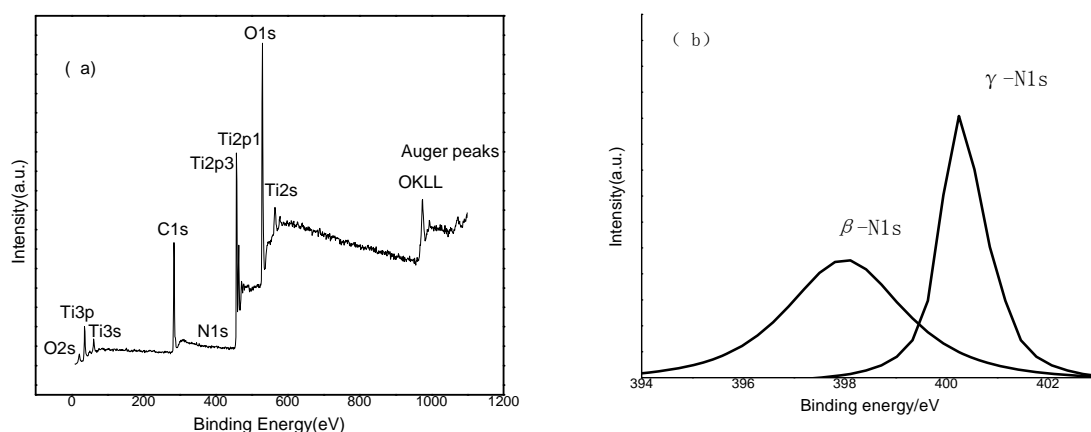
**Figure 3.** UV-Vis diffuse reflectance spectra of O-TiO<sub>2</sub> and UN-TiO<sub>2</sub>.

The ability of TiO<sub>2</sub> to absorb light usually changes after nonmetal doping [16]. Fig. 3 shows the diffuse reflectance spectra over the wavelength range of 300–700 nm for O-TiO<sub>2</sub> and UN-TiO<sub>2</sub>. It is clear that both samples have strong absorption in the ultraviolet region. UN-TiO<sub>2</sub> exhibits stronger absorbance intensity in the visible light region compared to O-TiO<sub>2</sub>, however, it is still weak compared to that in the ultraviolet. Compared to O-TiO<sub>2</sub>, UN-TiO<sub>2</sub> shows an obvious red shift at the absorption edges around 400 nm and a shoulder peak at longer wavelengths. Although the band gap energy of the samples was not ascertained, it was identified that the band gap of UN-TiO<sub>2</sub> could be greatly narrowed as a result of the red shift displayed by the UN-TiO<sub>2</sub> catalyst. These features further confirm mixing of the 2p states of the doped N anion with the O2p states, which is responsible for narrowing of the band gap energy of the titanate and the red shift of the valence band edge [10]. As mentioned earlier, ultrasonic cavitation provides a highly unusual and reactive chemical environment, i.e. extreme pressure and high temperature. The sol-gel method enhanced by ultra sonication therefore facilitates incorporation of N atoms into the TiO<sub>2</sub> lattice during preparation.

### 3.4. XPS

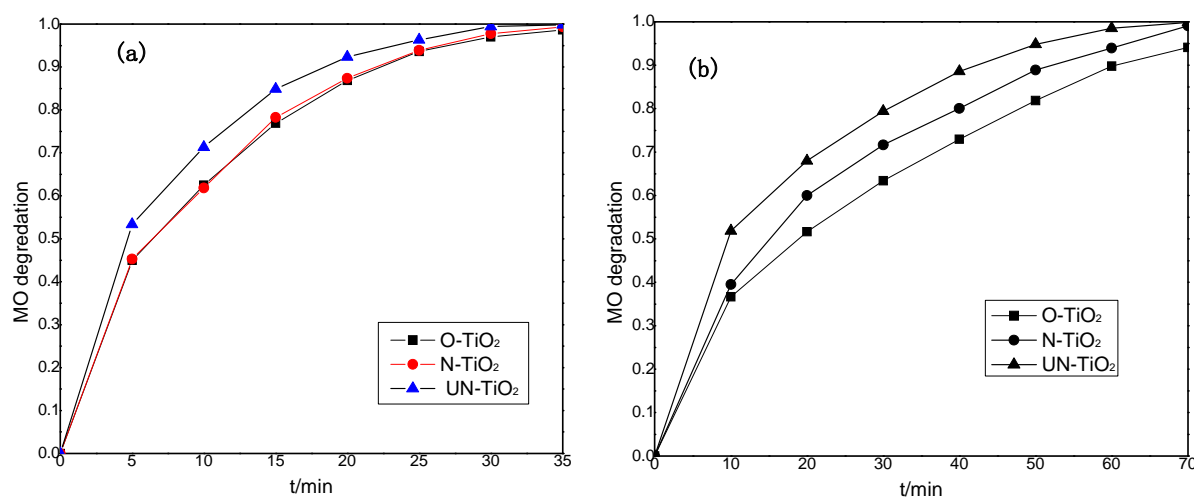
To identify the atom level doping of N in UN-TiO<sub>2</sub>, XPS analyses were carried out. Fig. 4 shows the XPS survey spectrum and the high-resolution spectra of the N1s region of the UN-TiO<sub>2</sub> sample. As shown in Fig. 4a, UN-TiO<sub>2</sub> contains a small amount of N atoms (binding energies between 397 and

401 eV). Two XPS peaks at binding energies of 397.3 and 400.1 eV are observed in Fig. 4b. Different N1s peak positions represent various forms of UN-TiO<sub>2</sub>. Assignment of N1s XPS peaks has been under dispute. As reported by Irie and Saha, N1s peaks can be decomposed into two contributions corresponding to different chemical states. One is attributed to  $\beta$ -N1s (binding energy at approximately 397eV), which belongs to N1s of TiN, the other to molecularly chemisorbed  $\gamma$ -N1s (binding energy at approximately 400 eV) [17]. The peak at around 400.00 eV has been frequently observed for N-TiO<sub>2</sub> materials [18]. At least one kind of nitrogen doping in the N-TiO<sub>2</sub> sample was therefore believed to be responsible for the visible light photoactivity.



**Figure 4.** XPS survey spectrum (a) and N1 score level (b) of sample.

### 3.5. Photocatalytic activity



**Figure 5.** Photocatalytic decomposition of MO under UV light (a) and visible light (b)

To explore the photocatalytic activity of samples, their degradation of MO under visible and UV light was investigated (Fig. 5). Under UV light irradiation, UN-TiO<sub>2</sub> could degrade 53 and 99% MO in 5 and 30 min, respectively. The photocatalytic activity of N-TiO<sub>2</sub> under UV light exceeded that of O-TiO<sub>2</sub> and N-TiO<sub>2</sub>. As shown in Fig. 5b, the decomposition rate of UN-TiO<sub>2</sub> towards MO under visible light irradiation is significantly enhanced compared to O-TiO<sub>2</sub> and N-TiO<sub>2</sub>. In particular, UN-TiO<sub>2</sub> could degrade 99% MO in 60 min, whereas O-TiO<sub>2</sub> could decompose only 88%. The enhanced UV photocatalytic performance of UN-TiO<sub>2</sub> could be attributed to the fact that ultra sonication creates a

unique environment for the hydrolysis of titanium lakeside, decreases the grain and particle size of  $\text{TiO}_2$ , and increases surface area, as indicated by the TEM results shown in Fig. 2. The lifetime of photogenerated electrons and holes can therefore be increased, which led to higher photocatalytic activity. The high visible photocatalytic activity of UN- $\text{TiO}_2$  is due to nitrogen doping, as indicated by the XPS results shown in Fig. 4, which is responsible for the red-shifted absorption edge of  $\text{TiO}_2$  [19](as indicated by the DRS results shown in Fig. 3).

#### 4. Conclusion

Anatase form Nitrogen-doped  $\text{TiO}_2$  was synthesized by a sol-gel process under ultrasonic irradiation. Ultrasonication reduces the crystallite size, and reduce agglomeration between particles. UN- $\text{TiO}_2$  prepared under ultrasonic irradiation showed higher UV and visible photocatalytic activity, which was mainly attributed to its small particle size, high surface area, and extended light absorption range. In particular, MO decomposition by UN- $\text{TiO}_2$  under visible light reached 99% in 60 min, while that of pristine  $\text{TiO}_2$  prepared without doping or ultrasonic irradiation was only 88%.

#### 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; and the Young Project of Xuzhou Institute of Technology under Grant No. XKY2016231.

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