Microstructures, Optical Properties and Degradation Efficiency of Nitrogen-doped Titanium Dioxide to Automobile Exhaust

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Abstract. To understand the influence of nitrogen (N) dopant on phase structure, morphology, optical property, photocatalytic degradation of TiO2 to automobile exhaust (AE) under visible light irradiation, the N-doped TiO2 was first prepared, and then X-ray diffraction (XRD), transmission electron microscopy (TEM), ultraviolet-visible light diffuse reflectance spectra (UV-vis DRS) and photocatalytic degradation tests were conducted. Results indicated that only anatase phase was found in both pure TiO2 and N-doped TiO2, and the N doping improved the dispersity of TiO2. Also, the N doping increased the absorbance of TiO2 under UV and visible light, respectively. An obvious red shift was observed on UV-Vis DRS of pure and N-doped TiO2 samples, indicating that the spectral response range of TiO2 was expanded to visible light region, and the utilization efficiency of solar irradiance was increased. The prepared N-doped TiO2 nanoparticles with an N dopant content of 3.0% showed better optical properties. Finally, the N doping improved the photocatalytic activity of TiO2 to AE in the visible light region. Furthermore, the N-doped TiO2 presented lower degradation efficiency to CO than that to CO2 under visible light radiation. Thus, it is found that the degradation efficiency of TiO2 to AE can be increased by the N doping under visible light radiation.

1. Introduction
Automobile exhaust (AE) including NOx, HC, CO2, CO, etc. causes serious environmental pollution [1]. AE brings great harms to human health and ecological environments so that some photocatalytic technologies have been developed to purify AE. Among them, TiO2, as one of important photocatalysts, is utilized to chemically degrade AE and other air pollutants due to its advantages of high photoactivity, good stability, non-toxicity, low cost, etc [2].

However, owing to the high band gap energy of TiO2, it can only be excited by ultraviolet (UV) light in sunlight to exert the property of photocatalytic degradation. However, the UV light only occupies about 4% in the total solar radiation [3]. This not only causes the insufficient use of solar energy but also lowers the photocatalytic efficiency of TiO2. Another disadvantage of pure TiO2 is that the recombination of photo-generated carriers decreases the photocatalytic activity of TiO2 [4]. Therefore, it is meaningful to increase the photocatalytic efficiency of TiO2 under visible light which occupies about 45% of total solar radiation.

Currently, the transition metal or nonmetal doping can not only broaden the photoresponse range of
TiO₂, but also promote the generation of electron holes. It has become one of the important methods to improve the photocatalytic efficiency of TiO₂ [5]. Among them, the N-doped TiO₂ has been paid more efforts due to its lower preparation cost and high photocatalytic activity under visible light, and controllable synthesis [6]. The photocatalytic performances of N-doped TiO₂ to methylene blue under the irradiation of visible light were discussed by Ramchiary et al. [7]. Powell [8] used the N doping method of TiO₂ to increase the absorbance of visible light, improving the photocatalytic activity of TiO₂. Todorova [9] reported the N-doped TiO₂ showed higher degradation efficiency to NOₓ than pure TiO₂. Triantis et al. [10] claimed that energy states in N doping configuration were formed in the TiO₂ band gap.

Additionally, it is noted that the photocatalytic degradation mechanism of N-doped TiO₂ under the radiation of visible light has not been well understood. Also, few researches have been focused on photocatalytic degradation efficiency of N-doped TiO₂ nanoparticles to AE. The purpose of this study is to use the N element as a dopant for doping TiO₂, improving the degradation efficiency of TiO₂ to AE under visible light. For this, in this study, the N-doped TiO₂ nanoparticles were synthesized using the sol-gel method. Then the phase microstructure of prepared TiO₂ nanoparticles were tested using X-ray diffraction (XRD), and the micromorphology and dispersity of N-doped TiO₂ nanoparticles were characterized by the transmission electron microscopy (TEM). In addition, the optical performance of TiO₂ nanoparticles were analyzed by ultraviolet-visible light diffuse reflectance spectra (UV-vis DRS). Finally, the degradation tests were conducted to validate the photocatalytic activity of N-doped TiO₂ to AE under visible light.

2. Materials and Method

2.1. Synthesis of TiO₂ Samples

N-doped TiO₂ nanoparticles were prepared using the sol-gel method. The tetra-n-butyl titanate and carbamide were utilized as titanium and N precursor, respectively. Firstly, 17 mL tetra-n-butyl titanate and 30 mL absolute ethanol were blended for 30 min at room temperature, preparing the solution A. Secondly, 8 mL deionized water, 20 mL acetic acid and 28 mL anhydrous alcohol were stirred, and then a calculated amount of carbamide (the mole ratio of N/Ti was 1.0%, 2.0%, 3.0% and 4.0%, respectively.) were dropped and fully mixed, preparing the solution B.

Then, the solution B was slowly dropped into solution A, and was stirred using a magnetic stirrer at 30 °C, thus the transparent and uniform sol was obtained, and the sol was matured at room temperature for 7 days to prepare the gel. After that, the prepared gel was dried at 80 °C for 1 day, and was milled into powders and calcined at 400 °C for 2.5 h. The N-doped TiO₂ nanoparticles were obtained. The prepared samples were marked as TiO₂+NX (the X was the N dopant content). Based on the same approach, N-doped TiO₂ samples containing various N dopant contents were synthesized. However, the pure TiO₂ nanoparticles were synthesized without the carbamide in the mixed liquor in the second step.

2.2. Characterization Methods

The phase structures of prepared TiO₂ samples were tested by XRD (Ultima IV type, Rigaku, Japan) with a Cu-Kα radiation (λ=0.15418 nm). XRD patterns were recorded in the 2θ range of 10° - 80° at a rate of 2°/min. The applied current was 30 mA, and the accelerating voltage was 40 kV.

A field emission TEM (JEM-2100 (HR) type, JEOL, Japan) was utilized to characterized microstructures and morphology of TiO₂. Its lattice resolution was 0.14 nm, and the amplification times were 50-1500000, and the point resolution was 0.23 nm.

The DRS of TiO₂ samples were recorded by a UV-vis spectrophotometer (Lambda 950 type, PE, USA) coupled with an integrating sphere. The scanning range was 200–800 nm at a data interval of 1nm. The reference sample for baseline correction was BaSO₄ standard.

2.3. Photocatalytic Activity Tests

As shown in Fig.1, an experimental setup was used to validate the photocatalytic degradation efficiency of prepared TiO₂ to AE under visible light. The prepared TiO₂ samples were first evenly
scattered on a plate with 300 mm in both length and width, and then the plate was placed in the closed non-transparent reactor. The height of incandescent lamp was about 20 cm from the plate. AE was produced by a gasoline engine generator. Its exhaust pipe was connected with the closed reaction reactor. The degradation tests of TiO₂ to four constituents of AE were carried out under visible light. A vacuum pump connected to the reaction reactor was utilized to control the initial pressure of the closed reaction reactor.

Firstly, the vacuum pump started to run for 60 s. The gasoline engine was then started to produce AE until it run steadily. The intake valve was opened, and AE was introduced into the closed reaction reactor. The intake valve was closed when the initial content of each constituent of AE approached a stable value.

After that, the incandescent lamp was turned on to validate the photocatalytic activity of TiO₂ to each constituent of AE. The content change of each constituent of AE vs. the radiation time was recorded for 60 min by an AE analyzer (HPC506 type, Huapeng, China). In the radiation process of incandescent lamp, the contents of NOₓ, CO, HC and CO₂ were tested at the interval of 10 min.

Finally, the degradation efficiency of TiO₂ to each constituent of AE was taken as the evaluating index calculated by Eq. (1).

\[ \eta = \frac{(C_0 - C_{\text{end}})}{C_0} \]  

Where, \( C_0 \) was the initial content of each constituent, and \( \eta \) was the degradation efficiency, and \( C_{\text{end}} \) was the residual content of each constituent at the end of degradation reaction.

3. Results and Discussion

3.1. Phase Structure

XRD patterns of pure and N-doped TiO₂ are presented in Figure 2. As illustrated in Figure 2, the N-doped and pure TiO₂ samples show similar phase structures. The representative diffraction peaks are observed at 62.7°, 55.0°, 53.9°, 48.0°, 37.8° and 25.3°, which correspond to six crystal planes of (204), (211), (105), (200), (004) and (101), respectively. It is noticed that the typical diffraction peaks of the rutile phase of TiO₂ are not observed, and all N-doped TiO₂ samples show anatase phase based on the comparison with the JCPDS NO: 21-1272. This suggests that the synthesized TiO₂ samples have high purity and crystallinity.
Figure 2. Typical XRD Patterns of N-doped and Pure TiO$_2$ Samples

By comparison, the phase compositions of N-doped TiO$_2$ samples are almost unchanged when compared with that of pure TiO$_2$ sample. Also, it is observed that the peak positions of major diffraction peaks of N-doped TiO$_2$ samples are similar with those of pure TiO$_2$ nanoparticles, but the above diffraction intensities are slightly changed. Moreover, the diffraction peaks of N impurities in the XRD diffraction patterns are not found. This suggests that the N dopants are evenly dispersed in the crystal lattices of TiO$_2$ samples, and its effects on the microstructures of TiO$_2$ are ignorable. Therefore, the crystal phase microstructures of TiO$_2$ nanoparticles are not changed by the N dopant.

3.2. Morphology Changes
The influences of the N dopant on the morphology and dispersity of TiO$_2$ are analyzed by TEM images of pure and N-doped TiO$_2$ as illustrated in Figure 3. From Figure 3, the particle morphologies of pure and N-doped TiO$_2$ present no obvious changes, and still show the spherical nanoparticles. The crystallite sizes of pure and N-doped TiO$_2$ are in the range between 13 nm to 16 nm. This is consistent with the XRD test results. Additionally, the dispersity of TiO$_2$ nanoparticles is increased when the N dopant content is raised from 0 % to 4.0 %. This is because the N-doping lowers the TiO$_2$ agglomeration in the heat treatment process to increase the dispersibility of TiO$_2$ nanoparticles. Also, this improves the specific surface area of TiO$_2$ nanoparticles, which is beneficial to raise the photocatalytic degradation efficiency of N-doped TiO$_2$.

Figure 3. TEM Images of Pure and N-doped TiO$_2$ Nanoparticles

3.3. Optical Property
In order to discuss effects of different N dopant contents on optical performances of TiO$_2$ nanoparticles, the test results of UV-vis DRS of N-doped and pure TiO$_2$ samples are provided in Figure 4.
It is seen from Figure 4 that the absorbance of N-doped TiO$_2$ is obviously improved under visible light radiation as compared with that of pure TiO$_2$ samples. Moreover, the optical absorption edges of N-doped TiO$_2$ present a red shift toward high wavelength, and the TiO$_2$+N3.0% shows the most obvious red shift toward high wavelength. This implies that the N-doping expands the optical absorption edge of TiO$_2$ from UV light to visible light region. This is conductive to increase the photocatalytic degradation efficiency and extend the utilization range of TiO$_2$ nanoparticles. The reason for this is that the local intermediate band gap (N2p) energy level is formed by the introduced N dopant on the top of O2p valence band in the TiO$_2$ nanoparticles [11]. Electrons of the doping energy level can be activated to the conduction band of TiO$_2$, resulting in the long wave photons to be absorbed [12]. Therefore, the absorption spectrum range of TiO$_2$ is expanded to the visible light region and the absorption performance in the visible light region is increased.

3.4. Photocatalytic Degradation Efficiency to AE under Visible Light

Based on the above analysis results, it is found that TiO$_2$+N3.0% sample has better optical properties. Therefore, we only discussed the photocatalytic activity of TiO$_2$+N3.0% and pure TiO$_2$ to each constituent of AE under visible light. The changes in NOx and HC concentration are shown in Figure 5 during the photocatalytic degradation of TiO$_2$+N3.0% and pure TiO$_2$.

It is found from Figure 5 (a) that the photocatalytic degradation of TiO$_2$+N3.0% and pure TiO$_2$ to NOx are similar in the first 30 min, and then the degradation effects of TiO$_2$+N3.0% is much higher than that of pure TiO$_2$. As presented in Fig. 5 (b), TiO$_2$+N3.0% exhibits a better photocatalytic degradation performance to HC in the first 10 min, and then degradation effects of the two TiO$_2$ samples tend to be equal in the next 20 min, but TiO$_2$+N3.0% sample shows a better photocatalytic degradation performance in the last 30 min. This indicates that the N doping actually improves the photocatalytic degradation efficiency of TiO$_2$ to NOx and HC under visible light.

It is because the impurity levels in TiO$_2$ are produced due to the substitution of doped N for partial O element. The electronegativity differences between N and O element form oxygen vacancies
around the substituted position, leading to the crystal lattice distortion in TiO$_2$ [13]. This causes some defects to generate on the surface of crystal, thereby the recombination of photo-generated electrons and holes is inhibited and the photocatalytic active centers are increased simultaneously [14]. All these are beneficial to increase the photocatalytic degradation efficiency of TiO$_2$ to AE under visible light.

The changes in CO and CO$_2$ concentration are shown in Figure 6 during the photocatalytic degradation of TiO$_2$+N$_{3.0%}$ and pure TiO$_2$.

It is noted from Figure 6 (a) that the photocatalytic degradation efficiencies of TiO$_2$+N$_{3.0%}$ and pure TiO$_2$ to CO are not obviously improved on the whole, but the N-doped TiO$_2$ sample still presents a slightly higher photocatalytic degradation property to CO than that of pure TiO$_2$ sample. As illustrated in Figure 6 (b), the photocatalytic degradation efficiencies of TiO$_2$+N$_{3.0%}$ and pure TiO$_2$ to CO$_2$ are almost equal each other in the first 30 min, but the pure TiO$_2$ shows a lower degradation efficiency than that of TiO$_2$+N$_{3.0%}$ sample in the next 30 min.

This suggests that the photocatalytic activity of TiO$_2$+N$_{3.0%}$ to CO and CO$_2$ is higher than that of pure TiO$_2$ although the photocatalytic degradation efficiencies of TiO$_2$+N$_{3.0%}$ and pure TiO$_2$ samples to CO$_2$ and CO are not obviously increased. All these indicate that the N doping can increase the photocatalytic degradation efficiencies of TiO$_2$ to CO$_2$ and CO under visible light. The reasons for this are the band gap of TiO$_2$ is narrowed owing to the N doping, and the absorption range of TiO$_2$ to visible light is broadened to absorb more visible light energy and generate more electron holes [15]. Also, the electrons in activated state are more likely to jump and accelerate the transfer rate of electron interface, improving the photocatalytic degradation efficiency under visible light.

![Figure 6. Concentration Changes of CO and CO$_2$ under Visible Light Irradiation](image)

Table 1 provides the calculated results of photocatalytic degradation efficiencies of TiO$_2$+N$_{3.0%}$ and pure TiO$_2$ to each constituent of AE under visible light.

| TiO$_2$ samples      | Photocatalytic degradation efficiency (%) |
|----------------------|------------------------------------------|
|                      | CO | CO$_2$ | HC | NO$_x$ |
| Pure-TiO$_2$         | 1.5| 2.1    | 4.6| 16.7   |
| TiO$_2$+N$_{3.0%}$   | 3.7| 4.3    | 7.8| 25.2   |

From Table 1, it is found that the pure TiO$_2$ has limited photocatalytic degradation efficiencies to different constituents of AE under visible light. However, the photocatalytic degradation efficiencies of N-doped TiO$_2$ to different constituents of AE under visible light are distinctly increased. It is concluded that the N doping is a feasible approach to increase the photocatalytic degradation efficiency of TiO$_2$ to AE under visible light.

4. Conclusions

1. Only contain anatase phase is found in the prepared N-doped nanoparticles with a slight
distortion. As the N dopant content is raised from 0% to 4%, the dispersity of TiO\(_2\) nanoparticles is increased, improving the specific surface area and photocatalytic degradation efficiency of TiO\(_2\). The grain size range of TiO\(_2\) sample is 13-16 nm with a spherical shape.

2) N-doped TiO\(_2\) shows higher optical absorptions than pure TiO\(_2\) in UV light and visible light regions. A red shift to higher wavelength is seen on UV-Vis DRS due to the N doping of TiO\(_2\), leading to the decrease in band gap of TiO\(_2\). This causes TiO\(_2\) to absorb more visible light and increase the utilization efficiency of solar irradiance, increasing the degradation efficiency of TiO\(_2\).

3) The N doping improves the degradation efficiency and photocatalytic activity of TiO\(_2\) to AE under visible light. The N-doped TiO\(_2\) shows lower degradation efficiencies to CO\(_2\) and CO than those to NO\(_x\) and HC of AE. Also, the N-doped TiO\(_2\) shows lower photocatalytic activity to CO than to CO\(_2\).

4) It is concluded that the N dopant improves the photocatalytic degradation efficiency of TiO\(_2\) to each constituent of AE under visible light for air purification, and expands the application range of TiO\(_2\). These are beneficial to further develop the pollutant purification technology using N-doped TiO\(_2\) nanoparticles as raw materials of building coating, road pavement, etc. along the street.

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6. References

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