

Photocatalytic oxidation of NO_x over visible-light-responsive nitrogen-doped TiO_2

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Abstract—In order to utilize visible-light in photocatalytic conversion of NO_x , nitrogen atoms were doped in commercially available photocatalytic TiO_2 powders by impregnating method. The crystal structures of TiO_2 were not changed after calcination process. Analysis by X-ray photoelectron spectroscopy (XPS) indicated that N atoms were incorporated in the bulk phase of TiO_2 as N-Ti-O linkages. A significant shift of the absorption edge to a lower energy and a higher absorption in the visible-light region were observed. These N-doped TiO_2 powders exhibited photocatalytic activity of the oxidation of NO_x under visible-light irradiation. The sample mixed with 20 wt% ammonium carbonate and calcined in 600 °C showed best photocatalytic activity and its activity can be restored by rinsing with water after long-term operation.

Key words: Photocatalysis, Nitrogen Doped Titania, Visible-Light Induced, Nitrogen Oxides, Environment

INTRODUCTION

Nitrogen oxides (NO_x) such as nitric oxide (NO), nitrous oxide (N_2O), and nitrogen dioxide (NO_2) exhausted from internal combustion engines and furnaces are harmful atmospheric pollutants that can cause acid rain, photochemical smog, and greenhouse effects. Therefore, removing NO_x effectively has become a very important topic in the field of environmental protection.

Photocatalytic conversion over various photocatalysts, such as titanium dioxide (TiO_2) [1-3], zeolites incorporated with transition metal ions (Cu^+ , Ag^+ , Pb^{2+}) [4-7], was recently applied to remove atmospheric NO_x ; thereinto, TiO_2 became the most widely used photocatalyst because of its non-noxious and stable chemical properties. Researchers have fully studied the kinetics of this reaction [8] and used various materials as supporter to enhance the efficiency of TiO_2 under UV light irradiation [9-14]. However, titania can only be encouraged by UV light, which only accounts for 3-4% of the solar energy that reaches the earth because of its large band gap value of 3.2 eV.

In order to utilize the visible rays, which offer 45% of solar energy, researchers have done much work. One of the commonly used methods is doping with transition metal ions such as Cr, V, Fe and others by ion-implantation or the sol-gel method [15-19]. The substitution of metal ion for Ti^{4+} changes the electronic properties of TiO_2 and sufficiently reduces the energy band gap to absorb visible light. Titania that contains argentine, platinum, rhodium and gold either in the bulk or at the surface has also been reported to exhibit photocatalytic activity in visible light [20-23]. The injection of electrons from the sensitizer to TiO_2 improves photocatalytic activity in visible light.

Like other nonmetal atom-doped TiO_2 , nitrogen-doped TiO_2 exhibits good photocatalytic activity in visible light despite the fact that there is still dispute about its action mechanism, and its prepa-

ration method, such as sputtering [24] and mechanochemical method [25], is relatively complex.

In this study, nitrogen-doped TiO_2 was synthesized by a relatively simpler method (impregnating method) to investigate the activity in response to visible light and the consequent oxidation of nitrogen oxides. The relationship between the properties and the photocatalytic activity with visible-light for N-doped TiO_2 powders was discussed. Its stability for oxidation of NO_x was also tested.

MATERIALS AND METHODS

1. Chemicals

Commercially available TiO_2 (particle size: 20 nm; composition: 100% anatase) obtained from Tianjin chemical Co. was used as photocatalyst, and ammonium carbonate (purity higher than 99.5%) was used as nitrogen source for N-doping. Nitrogen dioxide standard gas (100 ppm, N_2 balance, from Tianjin chemical Co.) attenuated by purified air was used as air stream to provide NO_2 gas.

2. Methods

For the synthesis of N-doping TiO_2 , 6 g of TiO_2 powder was mixed with 10-25 wt% ammonium carbonate by adding various concentrations of ammonium carbonate solution (40 ml) and stirred at room temperature for 30 min. The mixture was dried completely under vacuum dryer and then calcined at various temperatures (400, 500, 600, and 700 °C) for a period of 1 h.

Transmission electron micrographs (TEM) were recorded with an electron microscope (JEOL, JEM-100CX) to investigate the nano-structure of the catalysts. X-ray diffraction (XRD) with Co KR radiation (PANalytical, X'Pert) was employed to analyze the crystal structure of the synthesized products. The crystallite size was determined from the broadening of the peaks by using Scherrer's equation. The chemical states of nitrogen in the samples were obtained from X-ray photoelectron spectroscopy (XPS) (PE, PHI-1600). A binding energy calibration was performed by using the C1s peak in the background as the reference energy. A diffuse-reflectance scanning spectrophotometer (PE, Lambda35) was employed to ob-

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tain the UV-visible absorption spectra of the powders. The reflectance data were converted to the absorbance values, based on the Kubelka-Munk theory.

An annular Pyrex glass reactor (volume: 1,319 cm³, seen in Fig. 1) composed of two quartz glass tubes with a height of 280 mm and diameters of 95, 55 mm, respectively, was used to conduct the oxidation of NO_x. The inner quartz tube was used to place lamps. Four pieces of glass (230 mm×55 mm) were spread by TiO₂ and ethanol suspension, dried in the ambient air and fixed on a plate in the annular area to provide photocatalysts for reaction. A blue light lamp emitting lights of wavelengths from 410 to 530 with the maximum light intensity of 440 nm, and a green light lamp emitting lights of wavelengths from 470 to 570 with the maximum light intensity of 540 nm were used as the source of light. In addition, a fluorescent lamp with a wavelength ranging from 300 to 700 nm was used to simulate natural illumination conditions. The spectrum of the light from the light source was obtained by using a spectrophotometer (Gangdong technology Co, WGD-6). The temperature rise due to light irradiation was less than 5 °C because the power of the lamps was only 8 W and the inner quartz tube assisted in insulating some heat.

NO_x was degraded at room temperature by using an air stream at a flow rate of 0.5 L/min and contained 2.0 ppm NO₂ as feed-

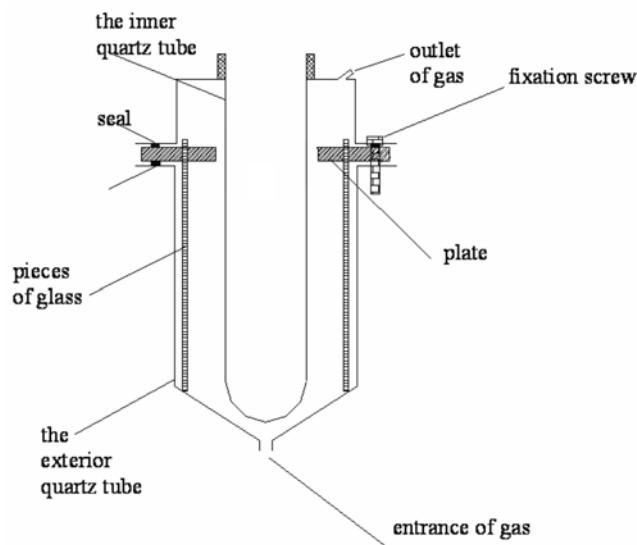


Fig. 1. Structure of reactor.

Table 1. Particle size and crystalline phase for N-doped TiO₂ at different calcination temperatures and quantity of ammonium carbonate

Sample	Calcinations temperature (°C)	Quantity of ammonium carbonate (wt%)	Crystallite size (nm)	Anatase crystalline phase (%)
N-TiO ₂	700	20	29.7	100
N-TiO ₂	600	20	24.1	100
N-TiO ₂	500	20	20.4	100
N-TiO ₂	400	20	19.7	100
N-TiO ₂	600	25	24.0	100
N-TiO ₂	600	15	24.1	100
N-TiO ₂	600	10	23.8	100
TiO ₂	-	0	19.1	100

stock. The retention time of the gas in the reactor was 2.64 min. The humidity and temperature of the air stream were measured by humidity and temperature meter (Center technology Corp, RS-232), which show that the reaction temperature is 20±5 °C. The NO₂ concentrations were continuously monitored with an on-line electrochemistry NO₂ analyzer (Junfang technology Co, GXH-1050D). The photocatalytic oxidation efficiency is decided by the formula below:

$$\eta = (C_i - C_o) / C_i \times 100\% \quad (1)$$

Where η is efficiency of photocatalytic oxidation in %; C_i is concentration of nitrogen oxides at reactor entrance; C_o is concentration of nitrogen oxides at reactor outlet.

TiO₂ powder removed from the glass after long-term operation was added to 40 mL distilled water and stirred at room temperature for 30 min. The suspension was filtered off and dried at 373 K. This procedure was repeated three times. The regenerated TiO₂ photocatalyst was characterized and its photocatalytic activity was valued by using the same method as the unused TiO₂.

RESULTS AND DISCUSSIONS

Fig. 2 shows the XRD patterns of the starting TiO₂ powder and the samples prepared by impregnating method. We can see that the impregnating and calcinations process did not change the crystal structures of TiO₂ which were still anatase. The anatase phase has

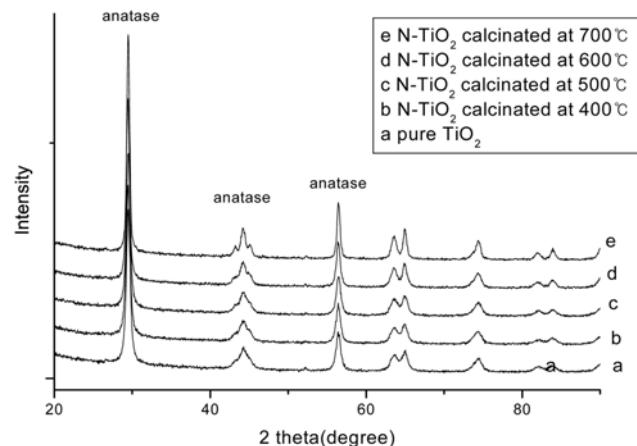


Fig. 2. XRD patterns of the starting TiO₂ powder and the samples prepared by impregnating method.

been retained without phase transformation to rutile even after the calcination temperature was increased to 700 °C. It has been reported that the transformation temperature of anatase to rutile is 700 °C [26]; thus mixing with ammonium carbonate seems to depress the phase transformation. The crystallite size of the N- TiO_2 particle was calculated by using the Scherrer equation and the values are given in Table 1.

As shown in Table 1, with the increasing of the calcination temperature, the particle size increased, which was caused by the agglomeration of particles at high temperatures. In addition, the crystallite size does not show much difference with the increasing of ammonium carbonate quantity, which suggests that mixing with ammonium carbonate did not affect the crystallite size of titanium dioxide. Besides, no change in the “d” space values (not shown) was observed, which means that N was introduced into the lattice without changing the average unit cell dimension in N-doped TiO_2 [27]. The morphologies of pure TiO_2 and N-doped TiO_2 were observed by TEM as shown in Fig. 3. It can be seen clearly from Fig. 3 that the particle sizes of pure TiO_2 and N-doped TiO_2 were 20 ± 2 nm and 25 ± 2 nm, which is consistent with XRD results. Besides, TEM images show that the agglomeration of N-doped TiO_2 is much severer than that of pure TiO_2 . Generally, the growing of crystallite size and the agglomeration of particles which cause the reducing of surface area are bad for photocatalysis. However, the photocatalytic oxidation efficiency of N-doped TiO_2 was much higher than that of pure TiO_2 , which implies that doping with N can enhance the photocata-

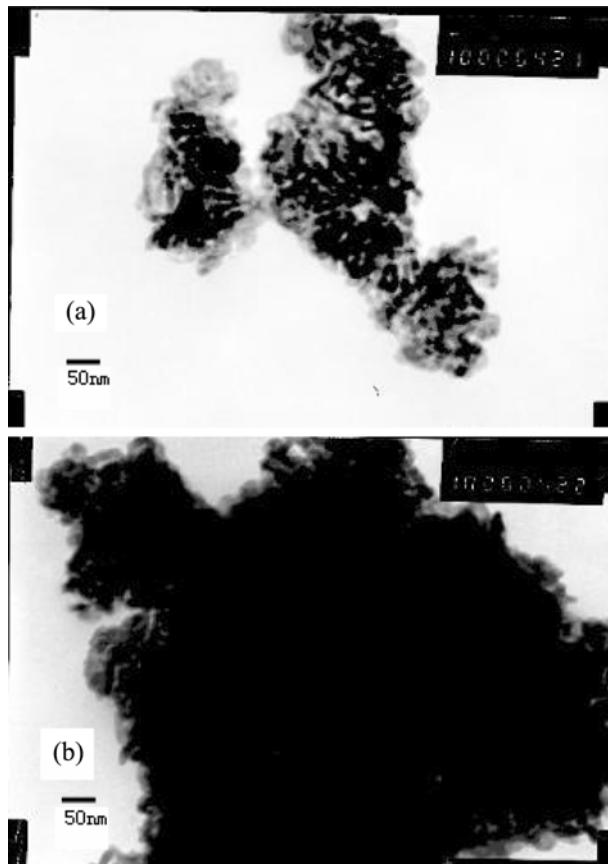


Fig. 3. TEM image of (a) pure TiO_2 , (b) TiO_2 mixed with 20 wt% ammonium carbonate and calcined at 600 °C.

lytic ability of TiO_2 notably and counteract the disadvantages caused by the doping process.

The UV-visible light absorption spectra of N- TiO_2 mixed with different amounts of ammonium carbonate and spectra as a function of calcination temperatures are shown in Fig. 4 and 5, respectively. It can be seen from Fig. 4 that the visible-light absorption is high and extends up to about 550 nm in the case of N- TiO_2 compared to that of pure TiO_2 . With the increasing amount of ammonium carbonate, the light absorption of N- TiO_2 in the visible region is enhanced because of the increasing of N atoms doping on the lattice of TiO_2 . Similarly, from Fig. 5, the visible absorption of N- TiO_2 decreases as the calcination temperature increases, which was also due to the fact that there was a decrease in the amount of N.

Fig. 6 shows X-ray photoelectron (XPS) spectra of the N 1 s profiles for pure TiO_2 and N-doped photocatalysts. Obviously, no peak is observed in pure TiO_2 , which indicates that no N atoms existed in pure TiO_2 . A single peak is observed in the spectrum of N-doped photo-

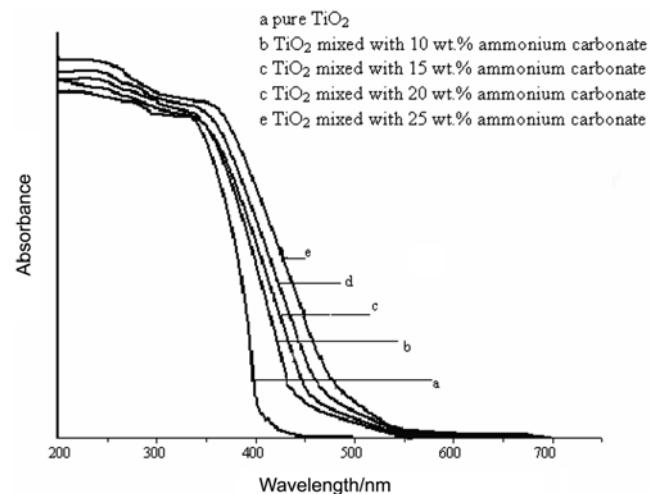


Fig. 4. UV-visible light absorption spectra of pure TiO_2 and N- TiO_2 mixed with different amount of ammonium carbonate.

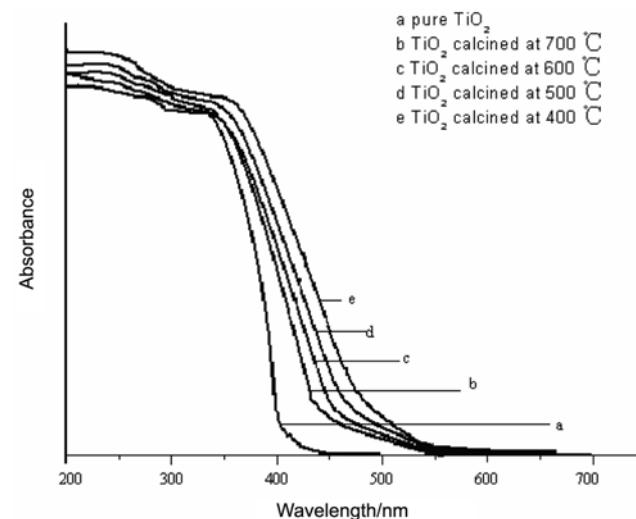


Fig. 5. UV-visible light absorption spectra of pure TiO_2 and N- TiO_2 calcined at different temperature.

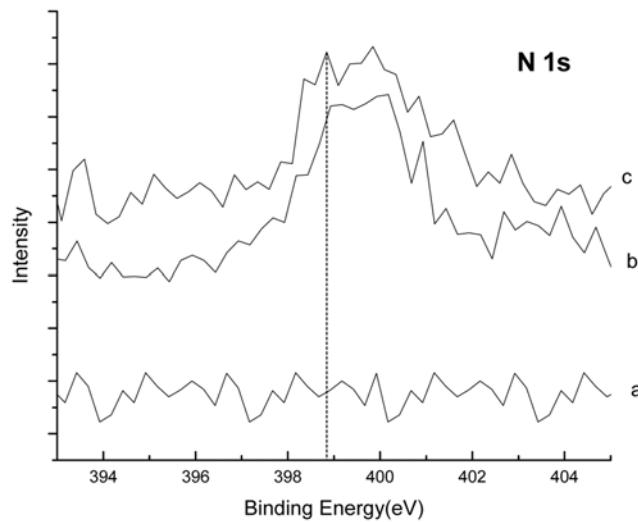


Fig. 6. X-ray photoelectron (XPS) spectra of the N1 s profiles for (a) pure TiO_2 , (b) TiO_2 mixed with 20 wt% ammonium carbonate and calcined in 700 °C and (c) TiO_2 mixed with 20 wt% ammonium carbonate and calcined in 600 °C.

catalysts around 399 eV and the peak intensity of sample (c) which showed better activity compared with sample (b) is also stronger. All of these phenomena suggest that the enhancing of visible photocatalytic activity is related with the peak around 399 eV. Several research groups investigated the N 1 s peak in XPS spectra during the oxidation of TiN and assigned the peaks as atomic β -N (396 eV) and molecularly chemisorbed γ -N₂ (400 and 402 eV) [28,29]. Based on these reports, researchers concluded that the peak at 396 eV corresponds to N atoms in Ti-N bonds, while a peak above 400 eV corresponds to N bound to O, C, or N atoms [27,30]. Therefore, a kind of linkage different from single Ti-N bonds and N-O, N-C, or N-N bonds must exist in the TiO_2 lattice. Generally, the electron density on nitrogen in the TiO_2 lattice might be reduced by the high

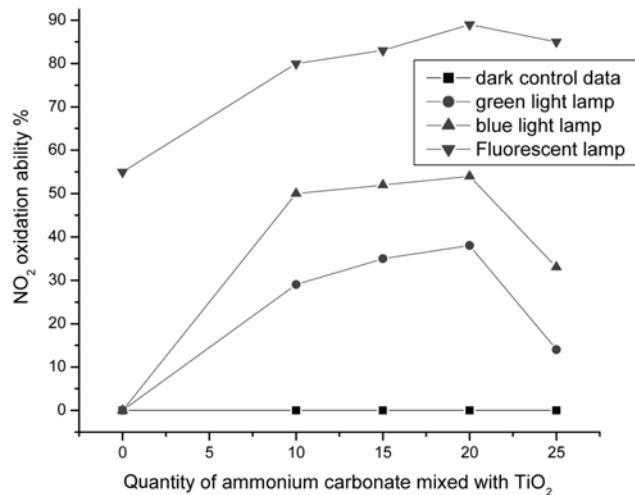


Fig. 7. Photocatalytic oxidation efficiency of NO_2 (%) over photocatalysts mixed with different quantity of ammonium carbonate and calcined at 600 °C (Catalyst loading=3 g, relative humidity=90%, feeding concentration of NO_2 =2.0 ppm, feeding flow rate=0.5 L/min).

electronegativity of oxygen, which would cause the increasing of binding energy of the Ti-N bond. Thus, Ti-N-O or N-Ti-O linkages may appear in TiO_2 lattice. Since it was reported that the presence of oxidized nitrogen such as Ti-O-N or Ti-N-O linkages should appear above 400 eV [31], which rules out the possibility of Ti-N-O linkages, we concluded that the peak observed in the present study at 399 eV is due to the N-anion incorporated in the TiO_2 as N-Ti-O structural feature. This result is similar to the conclusion of Sathish [27] and confirmed by the XRD patterns which do not show the formation of Ti-N crystallite.

The photocatalytic activity of the TiO_2 samples in the oxidation of NO_2 was studied in the end. As shown in Fig. 7, the removal rates of NO_2 over photocatalysts mixed with different quantity of ammonium carbonate were measured under blue, green light and simulated natural light from unicolor lamps and fluorescent lamp. With the increasing of the quantity of ammonium carbonate, the photocatalytic activity for oxidation of NO_x was enhanced under both unicolor and simulated natural light due to the N-Ti-O linkages which were formed in the impregnating and calcination process and caused the absorbance of visible-light. Although the absorbance of visible-light was toned up with the augment of ammonium carbonate, the photocatalytic oxidation efficiency for NO_2 decreased after reaching a peak at the 20 wt% ammonium carbonate (atomic ratio of Ti/N was 1/0.075 acquired by XPS measurements). From these, we can see that too many N atoms doping in the lattice of TiO_2 would destroy the structure of catalyst and impair the photocatalytic activity of TiO_2 notwithstanding the fact that N-Ti-O linkages increased the absorbance of visible-light.

Fig. 8 shows the correlation between the photocatalytic activity of the prepared TiO_2 samples and calcination temperature in the conversion of NO_2 under visible-light. Since the increase of calcination temperature would cause a decrease in the amount of N, it was concluded that only an appropriate amount of N doping on the lattice of TiO_2 could enhance the photocatalytic oxidation efficiency for NO_2 and 600 °C is the best calcination temperature, which is similar

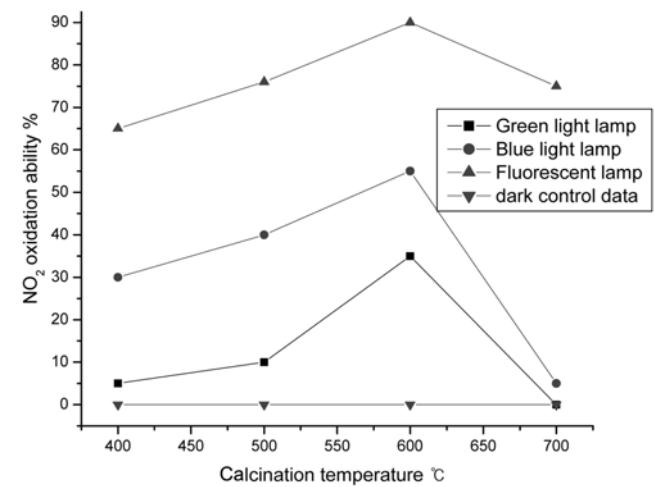


Fig. 8. Photocatalytic oxidation efficiency of NO_2 (%) over photocatalysts mixed with 20 wt% ammonium carbonate and calcined at various temperatures (Catalyst loading=3 g, relative humidity=90%, feeding concentration of NO_2 =2.0 ppm, feeding flow rate=0.5 L/min).

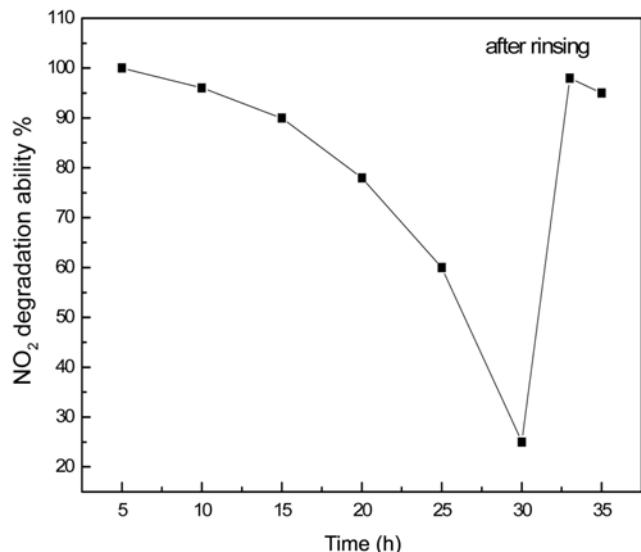


Fig. 9. Lifetime and regeneration of N-doped TiO_2 for oxidation of NO_x (Catalyst loading=3 g, relative humidity=90%, feeding concentration of NO_2 =2.0 ppm, feeding flow rate=0.5 L/min).

to the conclusion deduced by Fig. 7.

Lifetime and regeneration of Pt, N-codoped TiO_2 for oxidation of NO_x is shown in Fig. 9. We have found that the product of the photocatalytic reaction was nitric acid by Fourier Transform Infrared Spectrometer in previous experiments; thus, photocatalyst was deactivated after long-term operation because the NO_3^- ions adsorbed onto the surface of the catalyst and covered the active sites. However, the adsorbed NO_3^- ions were easily rinsed away with water, enabling the catalyst to be regenerated. The experimental results showed that over 90% of the photocatalytic activity was recovered after rinsing. Besides, the TEM images and X-ray photoelectron spectra (XPS) of the regenerated TiO_2 did not show much difference compared with these of unused N-doped TiO_2 , which indicated its stable chemical property.

CONCLUSION

Based on the above results, the following conclusions can be drawn:

1. Nitrogen-doped titania powders with homogeneous crystallite size (25 ± 2 nm) and visible-responsive photocatalytic activity were successfully prepared by relatively simple impregnating method. XPS results indicate the chemical environment of N is N-Ti-O linkages in the TiO_2 lattice, which is correlated with visible absorption.
2. The nitrogen-doped titania possessed absorption edge at 550 nm and showed excellent visible-light induced catalytic ability.
3. Appropriate amount of ammonium carbonate and calcinations temperature are significant for the doping process. The sample mixed with 20 wt% ammonium carbonate and calcined in 600 °C showed

the best photocatalytic activity.

4. This visible responsive N- TiO_2 indicates potential for air purification and energy-saving.

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