PHOTOCATALYTIC DEGRADATION OF NO_x OVER PLATINUM AND NITROGEN CODOPED TITANIUM DIOXIDE UNDER VISIBLE LIGHT IRRADIATION

Lin ZHOU[a,*], Xin TAN[b1], Lin ZHAO[b2] and Ming SUN[b3]
[a] *School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. China; e-mail: zhoulin00001@yahoo.com.cn*
[b] *School of Environment Science and Technology, Tianjin University, Tianjin 300072, P. R. China; e-mail: [1] tanxin@tju.edu.cn, [2] zhaolin@tju.edu.cn, [3] oliveree@126.com*

Received September 5, 2006
Accepted February 8, 2007

In order to utilize visible light and enhance the catalytic efficiency in photocatalytic conversion of NO_x, nitrogen and platinum atoms were doped in commercially available photocatalytic TiO_2 powders by impregnating and photodeposition methods, respectively. X-ray diffraction (XRD) showed that the crystal structures of TiO_2 were not changed after the doping 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 and Pt atoms were at the surface. A significant shift of the absorption edge to lower energy and higher absorption in the visible light region were observed. This Pt,N-codoped TiO_2 powder exhibited excellent photocatalytic activity and fairly stable chemical property for the degradation of NO_x under visible light irradiation. The sample mixed with 20 wt.% ammonium carbonate and doped with 0.5 at.% platinum atoms showed the best photocatalytic activity and its activity can be restored by rinsing with water after long-term operation.

Keywords: Photocatalysis; Nitrogen and platinum codoped titania; Visible light induced; Nitrogen oxides; Environment; Heterogeneous catalysis; Photochemistry.

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 is a kind of harmful atmospheric pollutants which 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)[1,2], zeolites incorporated with transition metal ions (Cu^+, Ag^+, Pb^{2+})[3–6], was recently applied to remove atmospheric NO_x, thereinto, TiO_2 became the most widely used photocatalyst because of its innoxious and stable chemical property. However, titania can only be encouraged by UV

Collect. Czech. Chem. Commun. 2007, Vol. 72, No. 3, pp. 379–391

doi:10.1135/cccc20070379

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 common used methods is doping with transition metal ions such as Cr, V, Fe and others by ion-implantation or the sol–gel method. 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[7–11].

The substitution of the lattice O^{2-} of the TiO_2 with nonmetal atoms, such as N [12,13], S [14,15], C [16] and B [17] is another common method. The newly formed intra-band gap states are found to be sufficiently close to the conduction band edge and lead to the appearance of an absorption band in visible light regions. Titania that contains silver, platinum, rhodium and gold either in the bulk or only at the surface has also been reported to exhibit photocatalytic activity in visible light[18–21]. The injection of electrons from the sensitizer to TiO_2 improves photocatalytic activity in visible light. Therefore, we deduce that loading nonmetal atoms-doped TiO_2 with noble metal would enhance the photocatalytic efficiency in conversion of NO_x under visible irradiation further despite the fact that no such research has been reported.

In this study, Pt,N-codoped TiO_2 was prepared by photodepositing Pt on the N-doped TiO_2 to investigate the activity in response to visible light and the consequent degradation of nitrogen oxides. The relationship between the properties and the photocatalytic activity with visible light for Pt,N-codoped TiO_2 powder was discussed. Its stability for degradation of NO_x was also tested.

EXPERIMENTAL

Chemicals

Commercially available TiO_2 (particle size: 20 nm; specific surface area: 80 m^2/g; composition: 100% anatase) obtained from Tianjin chemical Co. was used as photocatalyst. Ammonium carbonate and hexachloroplatinic acid (purity higher than 99.5%) were used as nitrogen and platinum source for 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.

Preparation of Catalyst

1. For the synthesis of N-doped TiO_2, 6 g of TiO_2 powder was mixed with 10–25 wt.% ammonium carbonate by adding various concentration of ammonium carbonate solution

(40 ml) and stirred at room temperature for 30 min. The mixture was dried completely under vacuum drying and then calcined at 873 K for 1 h.

2. To prepare Pt-doped TiO_2, 6.0 g of TiO_2 powder was mixed with 0.1–1.0 % H_2PtC1_6 by adding various amount 7.7×10^{-3} mol/l H_2PtC1_6 solution, then a little acetic acid was added into the mixture and the pH of the solution was adjusted to alkalescence by adding appropriate caustic soda solution. N_2 gas was bubbled into the suspension for 30 min to remove the dissolved O_2, after that the suspension was irradiated by a 500 W high-pressure Hg lamp for 4 h with continuous stirring. The suspension was filtered off, washed with water, and dried at 373 K.

3. For the synthesis of Pt,N-codoped TiO_2, pure TiO_2 was substituted with N-doped TiO_2 and the same photodeposition process for the preparation of Pt-doped TiO_2 was repeated.

Characterization of the Solids

Transmission electron micrographs (TEM) were recorded with a transmission electron microscope (FEI, Tecnai G2 F20) to investigate the nanostructure of the catalysts. X-ray diffraction (XRD) with CoKα radiation (PANalytical, X'Pert) was applied to analyze the crystal structure of the synthesized products. The crystallite size was determined from the broadening of the peaks using Scherrer's equation. Specific surface area and pore volume of the samples were estimated from N_2 adsorption at 77 K using a Sorptometric (NOVA-2000, Quantachrome) instrument. The chemical states of N and Pt atoms in the samples were obtained from X-ray photoelectron spectroscopy (XPS) (PE, PHI-1600). The binding energy calibration was performed using C 1s peak in the background as the reference energy. A diffuse reflectance scanning spectrophotometer (PE, Lambda35) was employed to obtain the UV-VIS absorption spectra of the powders. The reflectance data were converted to the absorbance values, based on the Kubelka–Munk theory.

Degradation of NO_x over TiO_2 Photocatalyst

An annular glass reactor (Fig. 1) composed of two quartz glass tubes with a height of 280 mm and diameters of 95 and 55 mm was used to conduct the degradation of NO_x. The inner

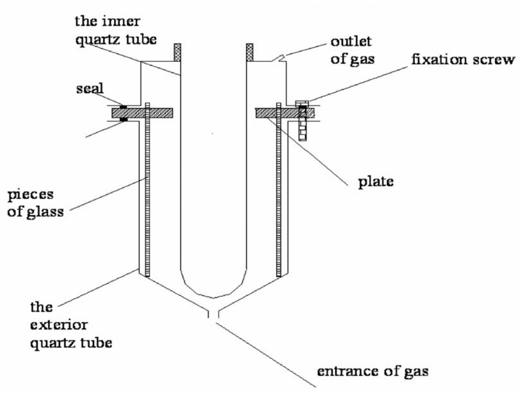

FIG. 1
Structure of reactor

quartz tube was used to place lamps. Four pieces of glasses (230 × 55 mm) were spread by TiO_2 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 nm with the maximum light intensity of 440 nm, and a green light lamp emitting lights of wavelengths from 470 to 570 nm 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 nature illumination conditions. The spectrum of the light from the light sources was obtained using a spectrophotometer (Gangdong technology Co., WGD-6). The temperature rise due to light irradiation was less than 5 K because the power of lamps was only 8 W and the inner quartz tube assisted in insulating some heat.

NO_x was degraded at room temperature using an air stream at a flow rate of 0.5 l/min and contained 2.0 ppm NO_2 as feedstock. The humidity and temperature of the air stream were measured by humidity temperature meter (Center technology Corp., RS-232). The NO_2 concentrations were continuously monitored by an on-line electrochemistry NO_2 analyzer (Junfang technology Co., GXH-1050D). The photocatalytic oxidation efficiency is decided by the formula

$$\eta = (c_\mathrm{i} - c_\mathrm{o})/c_\mathrm{i} \times 100\%$$

where η is the efficiency of photocatalytic oxidation in %, c_i is the concentration of nitrogen oxides at reactor entrance, c_o is the concentration of nitrogen oxides at reactor outlet.

Regeneration of TiO_2 Photocatalyst

TiO_2 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 for three times. The regenerated TiO_2 photocatalyst was characterized and its photocatalytic activity was valued using the same method as the unused TiO_2.

RESULTS AND DISCUSSIONS

Figure 2 shows the XRD patterns of the starting TiO_2 powder and doped TiO_2. From it, we can see that the doping processes did not change the crystal structures of TiO_2 which was still anatase. The crystallite size of TiO_2 was calculated using the Scherrer equation and the values are given in Table I along with other physical characteristics.

As is showed in Table I, the crystallite size does not show much difference with the increasing of ammonium carbonate and platinum. Besides, no change in the "d" space values (not shown) has been observed, which means that N atoms have been introduced into the lattice without changing the average unit cell dimension in N-doped TiO_2, while the Pt atoms may be only at the surface of Pt-doped TiO_2 (ref.[22]). In addition, particle size of TiO_2 was increased and the specific surface area was decreased after

TABLE I
Specific surface area, particle size and crystalline phase for TiO_2

Sample	Ammonium carbonate wt.%	Pt, at.%	Crystallite size, mm	Specific surface area, m^2/g	Anatase crystalline phase, %
N-TiO_2	10	0	23.8	58	100
N-TiO_2	15	0	24.1	59	100
N-TiO_2	20	0	24.1	58	100
N-TiO_2	25	0	24.0	58	100
Pt-TiO_2	0	0.1	25.3	58	100
Pt-TiO_2	0	0.2	25.3	58	100
Pt-TiO_2	0	0.5	25.3	58	100
Pt-TiO_2	0	1.0	25.4	59	100
Pt,N-TiO_2	20	0.5	25.3	58	100
TiO_2	0	0	19.1	80	100

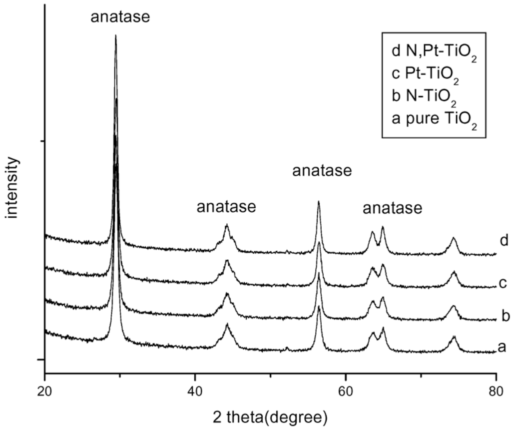

FIG. 2
XRD patterns of the starting TiO_2 powder (a), N-doped TiO_2 (b), Pt-doped TiO_2 (c) and Pt,N-codoped TiO_2 (d)

doping processes. Generally, the growing of crystallite size and the reducing of specific surface area are bad for photocatalysis. However, the photocatalytic oxidation efficiency of doped TiO_2 was much higher than that of pure TiO_2, which implies that the doping with N and Pt can enhance the photocatalytic ability of TiO_2 notably and counteract the disadvantages caused by doping process. The TEM images of Pt,N-codoped TiO_2 particles prepared by impregnating and photodeposition are shown in Fig. 3. The TEM images show that particle size of TiO_2 is 25 ± 2 nm, which was consistent with XRD results, while Pt particles are 5–10 nm in size.

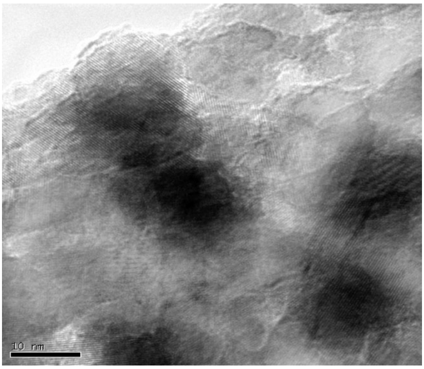

FIG. 3
TEM images of Pt,N-codoped TiO_2 particles

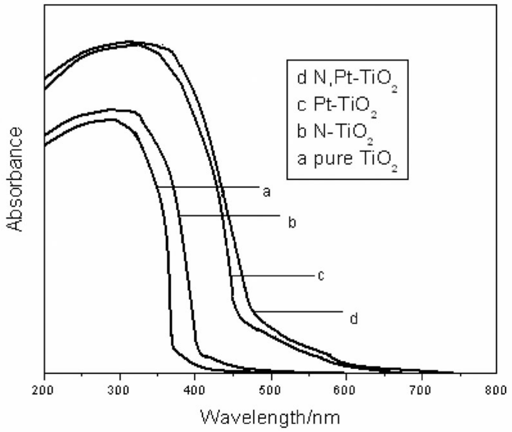

FIG. 4
The UV-VIS light absorption spectra of pure TiO_2 (a), N-doped TiO_2 (b), Pt-doped TiO_2 (c) and Pt,N-codoped TiO_2 (d)

The UV-VIS light absorption spectra of pure TiO_2, N- and Pt-doped TiO_2 and Pt,N-codoped TiO_2 are depicted in Fig. 4. It can be seen from Fig. 4 that the visible light absorption is higher and extends up to 550 nm in the case of N-TiO_2 compared to that of pure TiO_2 due to N atoms doping in the lattice of TiO_2 Besides, the absorption of Pt-doped TiO_2 is at slightly longer wavelengths and its intensity is also a little stronger compared to pure TiO_2 because the metallic Pt and PtO deposited on the surface of TiO_2 can absorb visible light and some energy levels can be produced in the band gap of TiO_2 by the dispersion of Pt nanoparticles in TiO_2. In addition, the absorption spectra of Pt,N-codoped TiO_2 does not show much difference with that of N-doped TiO_2 due to the fact that Pt atoms doped at the surface of TiO_2 do not affect the spectra of TiO_2 notably.

Figure 5 shows X-ray photoelectron spectra (XPS) of the spectra of the N 1s and Pt 4f profiles for Pt,N-codoped photocatalyst. A single peak is observed in the spectrum of Pt,N-codoped photocatalysts around 399 eV. Several research groups investigated the N 1s peak in XPS spectra during the oxidation of TiN and assigned the peaks as atomic β-N (396 eV) and molecularly chemisorbed γ-N_2 (400 and 402 eV)[22,23]. Based on these reports, researchers concluded that the peak at 396 eV corresponds to N atoms in Ti–N bonds, while the peak above 400 eV corresponds to N bound to O, C, or N atoms[24,25]. Therefore, there must be a kind of linkages different from single Ti–N bonds and N–O, N–C or N–N bonds in the TiO_2 lattice. Generally, the electron density on nitrogen in the TiO_2 lattice might be reduced by the high electronegativity of oxygen, which would cause the increasing of binding energy of 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 [26], 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[25] and confirmed by the XRD patterns which did not show the formation of Ti–N crystallite. In addition, Pt spectra show that there are two main Pt species: Pt^0 and $Pt^{II}O$ because peaks at 74.8 and 71.5 eV were assigned to Pt^0 and the peaks at 74.4 and 72.25 eV were correlated with PtO [27,28]. Although N_2 gas was bubbled into the suspension for 30 min to remove the dissolved O_2, there may still be a little O_2 in it, which would oxidize part of new generated Pt and produce PtO during photodeposition process.

The photocatalytic activity of the TiO_2 samples in the degradation of NO_x was also studied. As shown in Fig. 6, the removal rates of NO_x over photocatalysts mixed with different quantity of ammonium carbonate were measured under blue, green and simulated nature light from unicolor lamps and fluorescent lamp. With the increasing of the quantity of ammonium carbonate, the photocatalytic activity for degradation of NO_x was enhanced under both unicolor and simulated nature light due to the N–Ti–O linkages which were formed in impregnating and calcinations process and caused

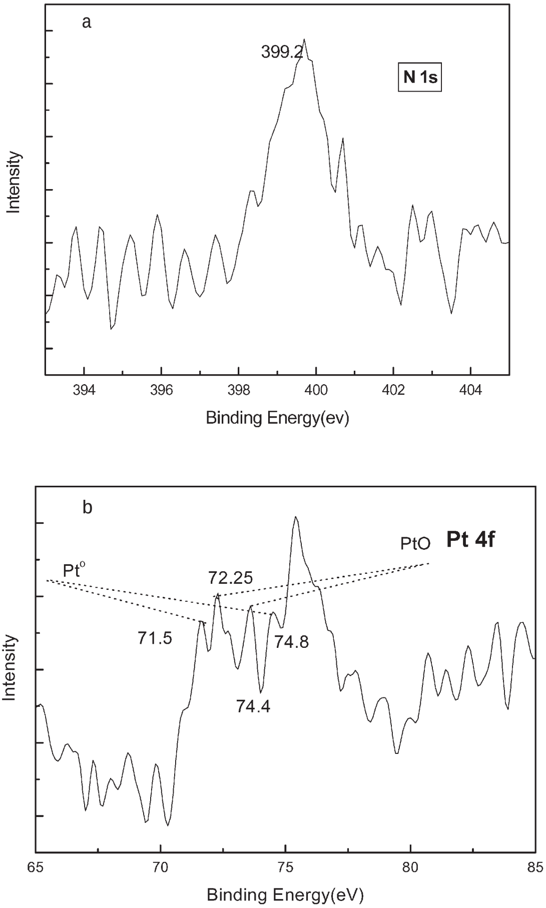

FIG. 5
XPS of the N 1s (a) and Pt 4f (b) profiles for Pt,N-codoped photocatalyst

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

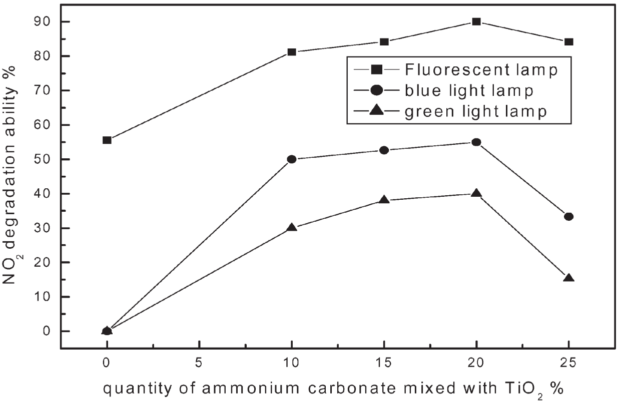

FIG. 6

The removal rates of NO_x over photocatalysts mixed with different quantity of ammonium carbonate (catalyst loading 3 g, relative humidity 90%, feeding NO_2 concentration 2.0 ppm, feeding flow rate 0.5 l/min). Flurorescent lamp (■), blue light lamp (●), green light lamp (▲)

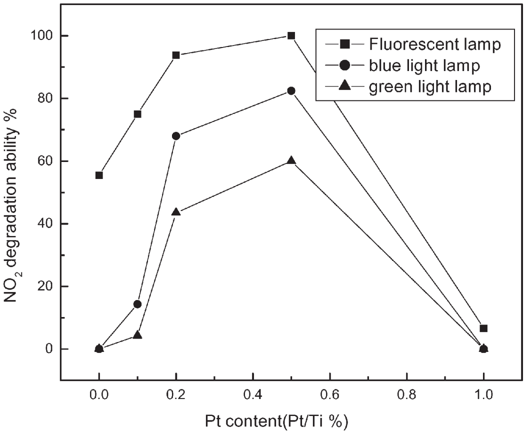

FIG. 7

The removal rates of NO_x over photocatalysts mixed with different quantity of Pt (catalyst loading 3 g, relative humidity 90 %, feeding NO_2 concentration 2.0 ppm, feeding flow rate 0.5 l/min). Flurorescent lamp (■), blue light lamp (●), green light lamp (▲)

measurements). From these, we can see that too many N atoms doping in the lattice of TiO_2 would shield the TiO_2 from the irradiation and impair the photocatytic activity of TiO_2 notwithstanding N–Ti–O linkages increased the absorbance of visible light.

Figure 7 shows the correlation between the photocatalytic activity of the prepared TiO_2 samples and quantity of Pt in the conversion of NO_x under visible light. Similarly as the phenomena depicted in Fig. 6, with the increasing quantity of Pt, the photocatalytic activity for degradation of NO_x was enhanced under both unicolor and simulated nature light because of the quick transfer of photogenerated electrons in TiO_2 semiconductor to the loaded Pt particles, resulting in a decrease in electron-hole recombination and efficient charge separation[29]. At very low Pt loading amount, the deposit size was probably too small to establish sufficient electrical contact for interfacial charge transfer to the reactant. As the Pt loading increases (0.1 to 0.5 at.% Pt), the Pt particles become larger and photoactivity is enhanced attributed to the additional electronic surface states formed under bandgap excitation. However, photoactivity decreases sharply when Pt loading amount on the TiO_2 surface increase to 1 at.% Pt due to the fact that Pt clusters became the center for the recombination of photogenerated holes and electrons with the increasing number of Pt deposits, thus reduced hole availability for the photooxidation. In addition, excessive coverage of the photosensitive surface by the platinum deposits may become more significant as the Pt loading increases, which also reduced the photoactivity.

Table II shows the removal efficiency of NO_x over Pt,N-codoped TiO_2, comparing with N- and Pt-doped TiO_2 samples which showed the best

TABLE II
The removal efficiency of NO_x over pure TiO_2, N- and Pt-doped TiO_2, and Pt,N-codoped TiO_2 (catalyst loading 3 g, relative humidity 90%, feeding NO_2 concentration 2.0 ppm, feeding flow rate 0.5 l/min)

Irradiation (lamp)	Samples			
	Pure TiO_2	N-doped TiO_2	Pt-doped TiO_2	Pt,N-codoped TiO_2
Fluorescent	55.5	90	100	100
Blue light	0	55.0	82.4	100
Green light	0	40.0	60.0	100

photooxidation efficiency. It can be clearly seen from Table II that the photooxidation efficiency of NO_x over Pt,N-codoped TiO_2 is not only much higher than that of pure TiO_2, but also higher than that of both N- and Pt-doped TiO_2 under both unicolor and simulated nature light. Combined with the discussion above, we can conclude that N–Ti–O linkages in the lattice of Pt,N-codoped TiO_2 formed in impregnating and calcinations process caused the absorbance of visible light and deposits of Pt at the surfaces of it provided more sites for photogenerated electrons to be efficiently transferred from the TiO_2 to its surface and interact with reactant, which enhanced the photogenerated electron-hole pair separation and improved the photocatalytic efficiency under visible irradiation notably.

Lifetime and regeneration of Pt,N-codoped TiO_2 for degradation of NO_x was shown in Fig. 8. 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 XPS of the regenerated TiO_2 did not show much difference comparing with these of unused Pt,N-codoped TiO_2, which indicated its stable chemical property.

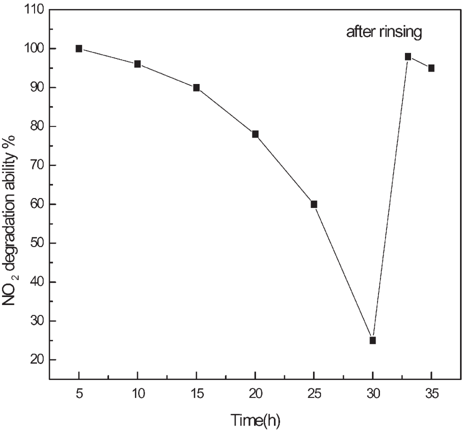

FIG. 8
Lifetime and regeneration of Pt,N-codoped TiO_2 for degradation of NO_x (catalyst loading 3 g, relative humidity 90%, feeding NO_2 concentration 2.0 ppm, feeding flow rate 0.5 l/min)

CONCLUSIONS

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

1. Pt,N-codoped titania powders with homogeneous crystallite size (25 ± 2 nm) and visible responsive photocatalytic activity were successfully prepared. XPS results indicated the chemical environment of N was as in N–Ti–O in the TiO_2 lattice while Pt existed at the surface of TiO_2 in the form of Pt^0 and $Pt^{II}O$.

2. These Pt,N-codoped titania possessed higher absorption in the visible light region and showed excellent visible light induced catalytic ability.

3. Appropriate amount of ammonium carbonate and platinum are significant for the doping process. The sample mixed with 20 wt.% ammonium carbonate and photodeposited 0.5 at.% platinum showed the best photocatalytic activity.

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

We acknowledge the financial support from National Nature Science Foundation of China.

REFERENCES

1. Ichiura H., Kitaoka T.: *Chemosphere* **2003**, *51*, 855.
2. Ao C. H., Lee S. C.: *Chem. Eng. Sci.* **2005**, *60*, 103.
3. Anpo M., Zhang S. G.: *Catal. Today* **1997**, *39*, 159.
4. Anpo M.: *Coord. Chem. Rev.* **1998**, *171*, 175.
5. Matsuoka M., Anpo M.: *Curr. Opin. Solid State Mater. Sci.* **2003**, *7*, 451.
6. Zhanpeisov N. U., Ju W. S.: *Res. Chem. Intermed.* **2003**, *29*, 407.
7. Anpo M., Takeuchi M.: *J. Catal.* **2003**, *216*, 505.
8. Radecka M., Wierzbicka M.: *Solid State Ionics* **2003**, *157*, 379.
9. Yamashita H., Anpo M.: *Catal. Surv. Asia* **2004**, *8*, 35.
10. Wu J. C. S., Chen C. H.: *J. Photochem. Photobiol., A* **2004**, *163*, 509.
11. Zhang X. W., Zhou M. H.: *Catal. Commun.* **2006**, *7*, 427.
12. Lindgren T., Mwabora J. M.: *J. Phys. Chem. B* **2003**, *107*, 5709.
13. Shu Y., Hi Y.: *Solid State Sci.* **2005**, *7*, 1479.
14. Umebayashi T., Yamaki T., Itoh H.: *Appl. Phys. Lett.* **2002**, *81*, 454.
15. Ohno T., Mitsui T., Matsumura M.: *Chem. Lett.* **2003**, *32*, 364.
16. Sakthivel S., Kisch H.: *Angew. Chem., Int. Ed.* **2003**, *42*, 4908.
17. Zhao W., Ma W. H., Chen C. C.: *J. Am. Chem. Soc.* **2004**, *126*, 4782.
18. Zang L., Macyk W.: *Chem.-Eur. J.* **2000**, *6*, 379.
19. Macyk W., Kisch H.: *Chem.-Eur. J.* **2001**, *7*, 1862.
20. Hu C., Lan Y. Q.: *J. Phys. Chem. B* **2006**, *110*, 4066.
21. Yu M. L., Tseng Y. H.: *Environ. Sci. Technol.* **2006**, *40*, 1616.
22. Saha N. C., Tompkins H. G.: *J. Appl. Phys.* **1992**, *72*, 3072.
23. Wu H. Z., Chou T. C.: *Thin Solid Films* **1990**, *191*, 55.

24. Nosaka Y., Matsushita M.: *Sci. Technol. Adv. Mater.* **2005**, *6*, 143.
25. Sathish M., Viswanathan B.: *Chem. Mater.* **2005**, *17*, 6349.
26. Gyorgy E.: *Surf. Coat. Technol.* **2003**, *173*, 265.
27. Barr T. L.: *J. Phys. Chem.* **1978**, *82*, 1801.
28. Hwang S., Lee M. C., Choi W.: *Appl. Catal., B* **2003**, *46*, 49.
29. Bamwenda G. R., Tsubota S., Nakamura T.: *J. Photochem. Photobiol., A* **1995**, *89*, 177.