Chin. J. Chem. Eng., **15**(6) 802—807 (2007)

Preparation of Nitrogen-doped TiO_2 Nanoparticle Catalyst and Its Catalytic Activity under Visible Light*

YU Huang(於煌)**, ZHENG Xuxu**(郑旭煦)****, YIN Zhongyi**(殷钟意)**, TAO Feng**(陶丰)**, FANG Beibei**(房蓓蓓) **and HOU Keshan**(侯苛山)
College of Environment and Bioengineering, Chongqing Technology and Business University, Chongqing 400067, China

Abstract N-doped TiO_2 nanoparticle photocatalysts were prepared through a sol-gel procedure using NH_4Cl as the nitrogen source and followed by calcination at certain temperature. Systematic studies for the preparation parameters and their impact on the structure and photocatalytic activity under ultraviolet (UV) and visible light irradiation were carried out. Multiple techniques (XRD, TEM, DRIF, DSC, and XPS) were commanded to characterize the crystal structures and chemical binding of N-doped TiO_2. Its photocatalytic activity was examined by the degradation of organic compounds. The catalytic activity of the prepared N-doped TiO_2 nanoparticles under visible light (λ>400nm) irradiation is evidenced by the decomposition of 4-chlorophenol, showing that nitrogen atoms in the N-doped TiO_2 nanoparticle catalyst are responsible for the visible light catalytic activity. The N-doped TiO_2 nanoparticle catalyst prepared with this modified route exhibits higher catalytic activity under UV irradiation in contrast to TiO_2 without N-doping. It is suggested that the doped nitrogen here is located at the interstitial site of TiO_2 lattice.
Keywords photocatalysis, TiO_2, visible light, nitrogen-doping, preparation

1 INTRODUCTION

Since the report of photoelectrochemical decomposition of water on titanium dioxide electrode in 1972[1], the chemical stability, nontoxicity, and high photocatalytic reactivity of TiO_2 has attracted tremendous attention. However, TiO_2 without doping is active only by irradiating with ultraviolet light because of its large band gap of 3.2eV (anatase). This band gap limits the use of the wide energy window of sun light because solar energy is the most important alternative energy source in the future[2]. To shift the optical response of catalytically active TiO_2 from ultraviolet (UV) to visible light, different studies have been carried out to modify TiO_2 to tune the band gap of TiO_2 for an absorption of visible light. Among these studies, nitrogen doping[3—6] is one of the most important methods for a promising application.

The reported nitrogen doping for TiO_2 mainly includes (1) sputtering TiO_2 target for several hours in an N_2/Ar gas mixture and then annealing in N_2 gas[7,8], (2) treating anatase TiO_2 powder in an NH_3/Ar atmosphere[7,9—11], and (3) a hydrolytic process using titanium alkoxide or chloride solution and an ammonia solution[12,13]. The first method needs expensive experimental facilities. The second and third routes are not environmentally friendly because of their use of ammonia. In principle, the combined sol-gel and calcination is an economic and reasonable method for the preparation of TiO_2 catalyst. However, there is an absence of a systematic investigation for the influence of preparation parameters on the formed crystal structures and the photocatalytic activity in this preparation strategy. Thus, here we used a modified sol-gel route for the preparation of N-doped TiO_2 and a relatively environmentally friendly NH_4Cl as nitrogen source. Multiple analytic techniques were used to monitor the intermediates and products at different stages of the preparation route. Preparation parameters including acidity of the solution of precursor, calcination temperature, and their impact on crystallization of TiO_2 xerogel mixed with NH_4Cl and photocatalytic activity of the N-doped TiO_2 were systematically studied. The dependence of the formed crystal structure and the photocatalytic activity on calcination temperature was revealed. The importance of pH of the precursor solution for the photocatalytic activity of the formed catalysts was demonstrated. An optimized preparation route was obtained, by which the prepared N-doped TiO_2 nanoparticle catalyst has obvious catalytic activity under visible light irradiation. Our studies suggest that the nitrogen is incorporated into interstitial sites which contribute to the appearance of catalytic activity under visible light irradiation and the obvious enhancement of activity under UV irradiation in contrast to TiO_2 without N-doping.

2 EXPERIMENTAL

2.1 Synthesis of N-doped TiO_2 catalyst

Tetra-butyl titanate [$Ti(OBu)_4$, 5ml, 97%] was dissolved in 95ml anhydrous alcohol. Into the solution of $Ti(OBu)_4$ was added 5ml NH_4Cl ($1mol\cdot L^{-1}$), dropwise, under stirring to carry out hydrolysis. The pH of the solution with NH_4Cl was controlled at a certain value. The gel was left for aging for one day at room temperature and subsequently dried at 70℃ for several hours. Finally, the dried material was calcined at dif-

Received 2006-12-21, accepted 2007-06-11.
* Supported by the Science and Technology Research Program of Chongqing Education Commission (KJ050702), and the Natural Science Foundation Project of Chongqing Science and Technology Commission (No.2007BB7208).
** To whom correspondence should be addressed. E-mail: zxx_chem@hotmail.com

ferent temperature to obtain N-doped TiO_2 nanoparticle catalyst with different doping level of nitrogen.

2.2 Analytical methods

The X-ray powder diffraction (XRD) patterns were recorded on a Shimadzu LabX-600 diffractometer with Cu K_α radiation (λ=0.1548nm). The size of the prepared nanoparticles was determined using the Scherrer formula $L=K\lambda/(\beta\cos\theta)$, where K is a constant of 0.89, λ is the wavelength characteristic of the Cu K_α radiation, β is the full width at half maximum (in radians), and θ is the angle at which the (100) peak appears. The mass percent of anatase in the product was obtained from the equation[14]: $X_A=[1+1.26(I_R/I_A)]^{-1}$, where X_A is the mass fraction of anatase in the mixture, I_A and I_R were obtained from the peak areas of anatase (101) and rutile (110) diffraction peaks, respectively. The morphology and sizes of the particles were examined using transmission electron microscopy (TEM) (Philips TECNAI 10 at 100kV). The diffuse reflectance infrared Fourier transform (DRIFT) spectra of the samples were measured on a Shimadzu IRPrestige-21 spectrometer. Thermal analysis was carried out on a differential scanning calorimeter (DSC) (Shimadzu, DSC-60) in N_2 atmosphere of 60ml·min^{-1} at a heating rate of 10℃·min^{-1} from room temperature to 600℃. N1s core level of the N-doped TiO_2 was measured with VG MultiLab 2000 system using Mg K_α (1253.6eV) radiation as X-ray source. The binding energies were calibrated with standard method.

2.3 Measurement of photocatalytic activity

The photocatalytic activity of the N-doped TiO_2 nanoparticle catalysts was characterized by photodegradation of methylene blue (MB) under UV light irradiation and 4-chlorophenol under visible light irradiation. For an examination of the catalytic activity under UV light irradiation, 100ml 20mg·L^{-1} MB aqueous solution with 0.05g catalyst was loaded in a glass container and mixed using a magnetic stirrer. The solution containing N-doped TiO_2 catalyst was left for 30min in a dark box and the solution was irradiated with a 30-W mercury lamp. In every 20min, 10ml solution was taken out and filtered through a 0.20mm membrane filter. To determine the catalytic activity of N-doped TiO_2 under visible light irradiation, 4-chlorophenol (13mg·L^{-1}) was used as a model compound. The visible 500-W xenon lamp was used as a visible light source upon blacking UV light by a 400nm glass filter. The concentrations of MB and 4-chlorophenol taken from the solution in a sequence were determined by UV absorbance spectrometer (751GD, Shanghai Analysis Apparatus Factory).

3 RESULTS AND DISCUSSION

3.1 Catalyst characterization

Figure 1 depicts the XRD patterns of the samples calcined at different temperatures. The N-doped samples exhibit an almost amorphous structure at 300℃, complete anatases structure at 400℃ and 500℃, and mixed structures of both anatase and rutile phases at

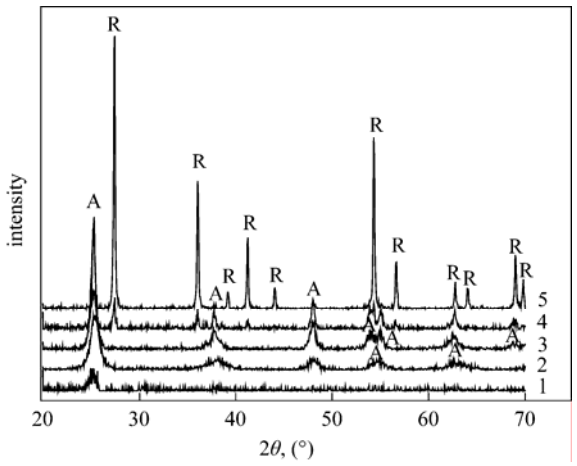


Figure 1 XRD patterns of N-doped TiO_2 calcined at different temperatures (A: anatase, R: rutile)
temperature, ℃: 1—300; 2—400; 3—500; 4—600; 5—700

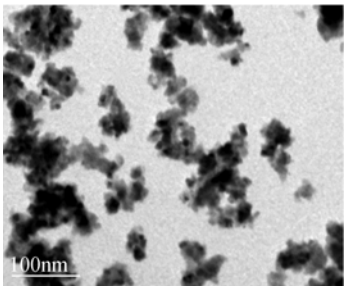
600℃ and 700℃. The temperature evolution shown in Fig.1 shows that the peak intensity of anatase increases and the width of the (101) diffraction peak of anatase phase (2θ=25.28°) becomes narrower with the increase of calcination temperature (from 400℃ to 500℃). This suggests that the particle size of N-doped TiO_2 nanoparticles increases from 400℃ to 500℃. Table 1 summarizes the phase structures and particle sizes of the prepared N-doped TiO_2 in the temperature range of 400—700℃. Clearly, calcination temperature plays a significant role in the formed crystal structure and particle size. Higher temperature favors the growth of rutile structure and produces N-doped TiO_2 nanoparticles with larger particle size. Thus, a fine control of calcination temperature is crucial for obtaining a pure phase of N-doped TiO_2.

Table 1 Influence of temperature on particle size and crystal phase of N-doped TiO_2

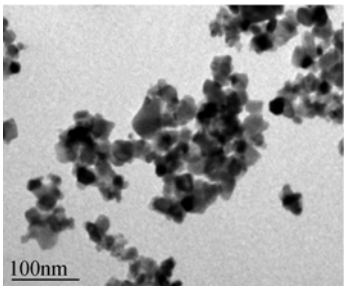
Temperature, ℃	Particle size, nm	Crystal phase
300	—	—
400	8.2	100%A
500	14.1	100%A
600	26.9(A), 33.3(R)	81.4%(A), 18.6%(R)
700	40.4(A), 66.4(R)	6.7%(A), 93.3% (R)

The particle sizes of the powders calcined at 400℃, 500℃,600℃,700℃ examined with TEM are 10—20nm, 15—30nm, 20—40nm, and 20—90nm, respectively. The obvious increase of particle size from 600℃ to 700℃ possibly results from aggregation at high temperature. The particle sizes examined with TEM are consistent with those calculated from XRD patterns listed in Table 1. Fig.2 is TEM images of the N-doped TiO_2 powders calcined at 500℃,600℃ and 700℃.

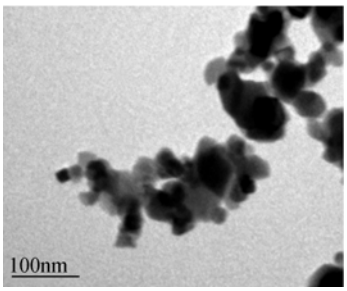
To understand the evolution of nitrogen source in the preparation route, DRIFT was used to obtain the



(a) T=500℃



(b) T=600℃



(c) T=700℃

Figure 2 TEM images of the N-doped TiO_2 nanocomposites calcined at 500℃, 600℃ and 700℃

vibrational signature of the intermediate before calcination. Fig.3 presents the DRIFT spectra of TiO_2 without calcination and TiO_2 xerogel mixed with NH4Cl without calcination. The wide band at 3100—3500cm^{-1} which appears in the spectrum of TiO_2 is because of the adsorbed water and the formed hydroxyl group. Compared with TiO_2 without N-doping, two new bands at 3132cm^{-1} and 1402cm^{-1}, attributed to NH_4^+ [15], appear in the spectrum of TiO_2 xerogel mixed with NH_4Cl. It shows that the NH_4^+ species are absorbed on the surface of TiO_2 before calcination and act as the nitrogen source for incorporation during calcinations[16]. The band at 450—470cm^{-1} appeared in the spectra of TiO_2 and TiO_2 xerogel mixed with NH_4Cl can be assigned to Ti—O stretching mode.

Figure 4 shows DSC curve of TiO_2 xerogel mixed with NH_4Cl without calcination. A big endothermic peak at about 102℃ was caused by desorption of the physisorbed water and alcohol. The relatively small endothermic peak at 303℃ possibly results from the desorption of unhydrolyzed $Ti(OBu)_2$ remained in the N-doped TiO_2 xerogel. The DSC curve also shows a significant exothermic peak at about 408℃, which is possibly because of the phase transformation from amorphous to anatase. There is no detectable exothermic peak at a temperature higher than 460℃, showing that TiO_2 gel prepared from sol-gel route containing-N has almost been crystallized into anatase upon calcination. Thus, 408℃ is the crystallization temperature of TiO_2 gel containing-N from amorphous to anatase. This result is consistent with the Ref.[12] and our XRD analysis described earlier.

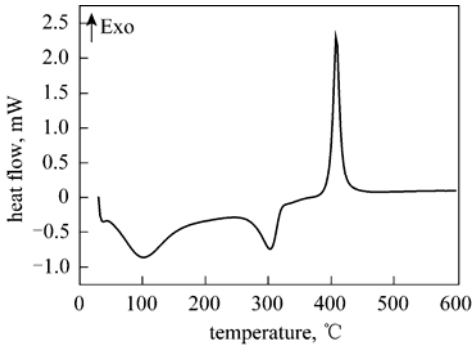


Figure 4 DSC curve of N-doped TiO_2

Figure 5 illustrates the light absorption properties of TiO_2 calcined at 500℃ and N-doped TiO_2 calcined at 500℃. The visible absorption spectra show that the N-doped TiO_2 is a photocatalyst with the capability of photocatalysis under visible light irradiation. The band gap of the samples was determined by the equation[17].

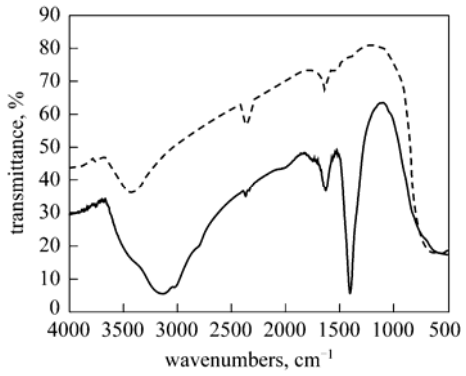


Figure 3 DRIFT spectra of undoped-TiO_2 and N-doped TiO_2

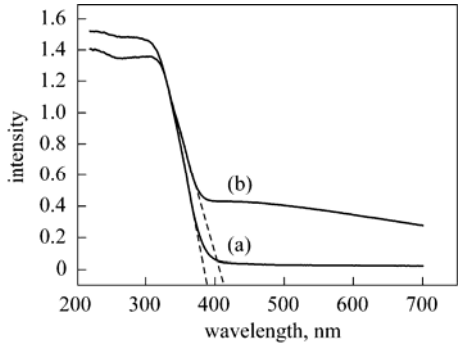


Figure 5 UV-Vis absorption spectra of TiO_2 (a) and N-doped TiO_2 (b) calcined at 500℃

$$E_g = 1239.8/\lambda$$

where E_g is the band gap (eV) and λ (nm) is the wavelength of the absorption edge in the spectrum. Compared with TiO_2 without N-doping, the band gap was changed from 3.20eV to 3.00eV of N-doped TiO_2. This change demonstrates a strategy for shaping photocatalysis by an atomic-level doping for nanocatalyst. In addition, the absorption spectra of the N-doped TiO_2 samples also showed a stronger absorption than TiO_2 without N-doping under UV irradiation, indicating that N-doping could be a promising approach for increasing the catalytic activity. The increase of the catalytic activity upon N-doping is different from the previous study[7,18]. This difference could result from our different preparation route and nitrogen source. Further study and mechanistic understanding is under investigation.

Figure 6(b) depicts the photoemission feature of the N1s core level of the prepared N-doped TiO_2 nanoparticle catalyst. The TiO_2 without N-doping is taken as a reference here [Fig.6(a)]. No observable N1s photoemission feature for TiO_2 calcined at 500℃, as shown in Fig.6(a), shows that molecular nitrogen in air cannot be incorporated into TiO_2 lattice under calcination at 500℃. This is so though N_2 is a nitrogen source for the growth of $TiO_{2-x}N_x$ film by sputtering TiO_2 target in N_2/Ar mixture gas and annealed to high temperature in N_2 gas[7,8]. However, the observation of an obvious peak at about 398.6eV as seen in Fig.6(b) suggests that nitrogen of NH_4^+ is incorporated into TiO_2 lattice upon calcination. Notably, a peak of N1s core level at 396.7eV was reported for N-doped TiO_2 by other group using different preparation route[19]. The doped nitrogen was understood as a substitute for oxygen atom of TiO_2 lattice. Compared with the low-binding energy at 396.7eV resulting from electron transfer from Ti with low electronegativity to N atom, the doped nitrogen of our samples has a higher binding energy at 398.6eV. This difference suggests that the doped nitrogen in TiO_2 prepared with our route has different structural geometry and chemical binding in TiO_2 lattice. It possibly rationalizes the different catalytic activity under UV light irradiation described earlier in contrast to the previous studies[7,18]. It is suggested that the doped nitrogen atoms in our sample are possibly located at interstitial sites, which has a weak binding with Ti atoms. The N1s binding energy seen in Fig.6(b) is consistent with that of NH_x-containing compound[20], indicating that NH_4^+ does not completely decompose into nitrogen atom during calcination.

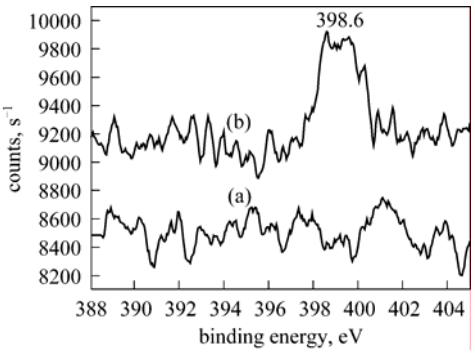


Figure 6 N1s XPS spectra of TiO_2 (a) and N-doped TiO_2 (b) calcined at 500℃

3.2 Influential factors of photocatalytic activity

3.2.1 *Influence of calcination temperature on photocatalytic activity*

Figure 7 presents the photocatalytic activity of different N-doped TiO_2 samples under UV irradiation as a function of calcination temperature. MB is used as a probe for determining the catalytic activity under UV irradiation. The photocatalytic activity of the samples increases with the increase of calcination temperature from 300℃ to 500℃. At 500℃ it reaches the maxima because of a complete crystallization of anatase at this temperature. However, the catalytic activity of N-doped TiO_2 decreases obviously with the increase of calcination temperature from 500℃ to 700℃. This is consistent with the fact that anatase is more photocatalytically active than rutile phase, and more anatase was converted into rutile phase at a higher calcination temperature between 500℃ and 700℃ (Fig.1 and Table 1). The importance of calcination temperature is demonstrated here.

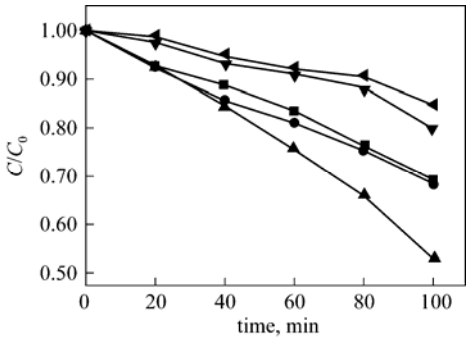


Figure 7 Photoactivity of N-doped TiO_2 calcined at different temperatures under UV light
temperature, ℃: ■300; ●400; ▲500; ▼600; ◀700

3.2.2 *Influence of pH of the solution of precursor on photocatalytic activity*

Figure 8 shows that the photocatalytic activity of N-doped TiO_2 is prepared in a solution of precursor with different acidity (pH＝2—5) and then calcined at 500℃. The photocatalytic activity of N-doped TiO_2 nanoparticle catalyst increases when the value of pH decreases from 5 to 3, at which it reaches a maxima. The possible reason is that the increase of H^+ concentration along with the decrease of pH restrains hydrolyzation of $Ti(OBu)_4$ and thereby results in the decrease of the crystal size of the prepared N-doped TiO_2 nanoparticles. However, pH cannot be too low. Too low pH such as 2 would result in a phase transformation from anatase to rutile[21], supported by the low photocatalytic activity of the samples prepared at pH＝2.

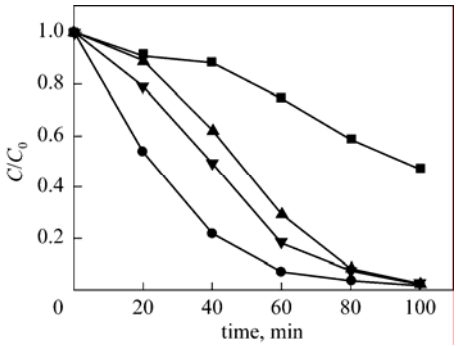


Figure 8 Photoactivity of N-doped TiO_2 prepared at different pH under UV light
pH: ■2; ●3; ▼4; ▲5

3.3 Visible light activity

The aforementioned systematic investigations show that the N-doped TiO_2 exhibits the largest catalytic activity under UV light irradiation at the calcination temperature of 500℃ and pH=3. To explore the visible light activity of N-doped TiO_2 nanoparticle catalyst prepared at this condition, 500-W xenon lamp with a 400nm cut-off filter was used as a visible light source. In order to avoid the dye-sensitized effect of MB, 4-chlorophenol was used as a new probe. The catalytic activity of undoped-TiO_2 and N-doped TiO_2 nanoparticles was examined (Fig.9). Obviously, N-doped TiO_2 can degrade 4-chlorophenol under visible light ($\lambda > 400$nm) irradiation with a 63.5% conversion upon 6h, whose visible light activity is little better than the reported activity[22]. TiO_2 without any doping could not degrade 4-chlorophenol under the same condition. Thus, the TiO_2 without N-doping is not catalytically active under visible light irradiation for this reaction. As implied by XPS data in Fig.6, the doped nitrogen is possibly located at interstitial sites, it may give rise to a midgap (N-2p) level slightly above the top of the (O-2p) valence band. The electron is transferred from the midgap band to conduction band of TiO_2 and thereby induces catalytic activity under visible light irradiation[4,9].

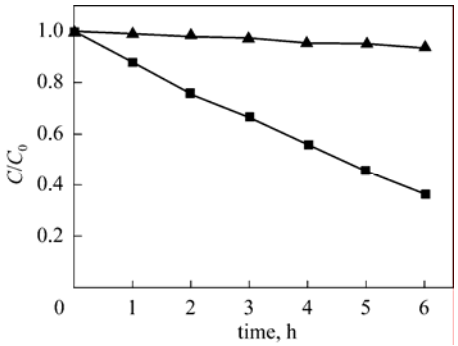


Figure 9 Photoactivity of TiO_2 and N-doped TiO_2 under visible light
■N-doped TiO_2; ▲TiO_2

4 CONCLUSIONS

N-doped TiO_2 nanoparticle catalysts exhibiting photocatalytic activity under UV and visible light irradiation were successfully prepared by a modified sol-gel procedure using NH_4Cl as nitrogen source followed by calcination at a certain temperature. Our investigations revealed that the acidity (pH value) of the solution of precursor and the subsequent calcination temperature have a significant impact on the crystallization of xerogel and the particle size of the formed N-doped TiO_2 nanoparticle catalyst, and the photocatalytic activity. Systematical studies showed that N-doped TiO_2 nanoparticle catalyst prepared at a solution with pH=3 and calcination temperature of 500℃ has the largest photocatalytic activity. It is suggested that the NH_4^+ species were absorbed on the surface of TiO_2 gel at low temperature and subsequently incorporated into the TiO_2 lattice during calcination at high temperature. The N-doped TiO_2 exhibits higher activity than TiO_2 without N-doping under UV irradiation. N-doped TiO_2 nanoparticle catalyst has obvious visible light activity, evidenced by the degradation of 4-chlorophenol under visible light ($\lambda >$ 400nm) irradiation. However, the catalytic activity under visible light irradiation is absent for TiO_2 without N-doping. Further studies on the geometric structure and chemical binding of the doped nitrogen in the TiO_2 lattice are in progress.

REFERENCES

1 Fujishima, A., Honda, K., "Electrochemical photolysis of water at a semiconductor electrode", *Nature*, **238**, 37—38(1972).
2 Gole, J.L., Stout, J.D., Burda, C., Lou, Y., Chen, X., "Highly efficient formation of visible light tunable $TiO_{2-x}N_x$ photocatalysts and their transformation at the nanoscale", *J. Phys. Chem. B*, **108**(4), 1230—1240(2004).
3 Wang, Z., Cai, W., Hong, X., Zhao, X., Xu, F., Cai, C., "Photocatalytic degradation of phenol in aqueous nitrogen-doped TiO_2 suspensions with various light sources", *App. Catal. B*, **57**(3), 223—231(2005).
4 Nakamura, R., Tanaka, T., Nakato, Y., "Mechanism for visible light responses in anodic photocurrents at N-doped TiO_2 film electrodes", *J. Phys. Chem. B*, **108**(30), 10617—10620(2004).
5 Jang, J.S., Kim, H.G., Ji, S.M., Bae, S.W., Jung, J.H., Shon, B.H., Lee, J.S., "Formation of crystalline $TiO_{2-x}N_x$ and its photocatalytic activity", *J. Solid State Chem.*, **179**(4), 1067—1075(2006).
6 Yin, S., Ihara, K., Komatsu, M., Zhang, Q., Saito, F., Kyotani, T., Sato, T., "Low temperature synthesis of $TiO_{2-x}N_y$ powders and films with visible light responsive photocatalytic activity", *Solid State Commun.*, **137**(3), 132—137(2006).
7 Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K., Taga, Y., "Visible-light photocatalysis in nitrogen-doped titanium oxides", *Science*, **293**(5528), 269—271(2001).
8 Wong, M.S., Chou, H.P., Yang, T.S., "Reactively sputtered N-doped titanium oxide films as visible-light photocatalyst", *Thin Solid Films*, **494**(1/2), 244—249(2006).
9 Irie, H., Watanabe, Y., Hashimoto, K., "Nitrogen-concentration dependence on photocatalytic activity of $TiO_{2-x}N_x$ powders", *J. Phys. Chem. B*, **107**(23), 5483—5486(2003).
10 Kosowska, B., Mozia, S., Morawski, A.W., Grzmil, B., Janus, M., Kalucki, K., "The preparation of TiO_2-nitrogen doped by calcination of TiO_2 middle dot xH_2O under ammonia atmosphere for visible light photocatalysis", *Sol. Energ. Mat. Sol. C.*, **88**(3), 269—280(2005).

11 Mozia, S., Tomaszewska, M., Kosowska, B., Grzmil, B., Morawski, A.W., Kalucki, K., "Decomposition of non-ionic surfactant on a nitrogen-doped photocatalyst under visible-light irradiation", *App. Catal. B*, **55**(3), 195—200(2005).

12 Sato, S., Nakamura, R., Abe, S., "Visible-light sensitization of TiO_2 photocatalysts by wet-method N doping", *Appl. Cata. A*, **284**(1/2), 131—137(2005).

13 Liu, Y., Chen, X., Li, J., Burda, C., "Photocatalytic degradation of azo dyes by nitrogen-doped TiO_2 nanocatalysts", *Chemosphere*, **61**(1), 11—18(2005).

14 Spurr, R.A., Myers, H., "Quantitative analysis of anatase-rutile mixtures with an X-ray diffractometer", *Anal. Chem*., **29**(5), 760—762(1957).

15 Ihara, T., Miyoshi, M., Iriyama, Y., Matsumoto, O., Sugihara, S., "Visible-light-active titanium oxide photocatalyst realized by an oxygen-deficient structure and by nitrogen doping", *App. Catal. B*, **42**(4), 403—409(2003).

16 Kuroda, Y., Mori, T., Yagi, K., Makihata, N., Kawahara, Y., Nagao, M., Kittaka, S., "Preparation of visible-light-responsive $TiO_{2-x}N_x$ photocatalyst by a sol-gel method: Analysis of the active center on TiO_2 that reacts with NH3", *Langmuir*., **21**(17), 8026—8034(2005).

17 O'Regan, B., Gratzel, M., "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films", *Nature*, **353**(6346), 737—740(1991).

18 Wang, Z.P., Cai, W.M., Hong, X.T., Zhao, X.L., Xu, F., Cai, C.G., "Photocatalytic degradation of phenol in aqueous nitrogen-doped TiO_2 suspensions with various light sources", *Appl. Catal. B*, **57**(3), 223—231(2005).

19 Saha, N.C., Tompkins, H.G., "Titanium nitride oxidation chemistry: An X-ray photoelectron spectroscopy study", *J. Appl. Phys*., **72**(7), 3072—3079(1992).

20 Souto, S., Alvarez, F., "The role of hydrogen in nitrogen-containing diamondlike films studied by photoelectron spectroscopy", *Appl. Phys. Lett*., **70**(12), 1539—1541(1997).

21 Chen, X., Gu, G., "Study on synthesis of nanometer TiO_2 crystal from organic compound in liquid phase at normal pressure and low temperature", *Chin. J. Inorg. Chem*., **18**(7), 749—752(2002).

22 Sakthivel, S., Kisch H., "Photocatalytic and photoelectrochemical properties of nitrogen-doped titanium dioxide", *Chemphyschem*, **4**(5), 487—490(2003).