Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 2011, 23(11) 1919–1924
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Visible light responsive N-F-codoped TiO_2 photocatalysts for the degradation of 4-chlorophenol

Xiaohong Li[1], Haidong Zhang[1,2], Xuxu Zheng[1,2,*], Zhongyi Yin[2], Le Wei[2]

1. Laboratory of Applied Catalysis, Engineering Research Centre for Waste Oil Recovery Technology and Equipment, Ministry of Education, Chongqing Technology and Business University, Chongqing 400067, China. E-mail: xuxuzheng@ctbu.edu.cn
2. Environmental and Biological Engineering Institute, Chongqing Technology and Business University, Chongqing 400067, China

Received 22 December 2010; revised 15 April 2011; accepted 25 April 2011

Abstract

N-F-codoped TiO_2 (NFTO) photocatalysts were synthesized by a simple sol-gel process with tetrabutyl titanate ($Ti(OBu)_4$) as the precursor of TiO_2 and ammonium fluoride (NH_4F) as the source of N and F. The synthesized photocatalysts were investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) and photodegradation reaction tests of 4-chlorophenol under visible light irradiation to understand the relationship between the structure of NFTO catalyst and corresponding photocatalytic activity. The crystal phase and particle size of catalysts were found to be largely affected by the calcination temperature. In addition, N-F-codoping could inhibit phase transition of TiO_2 from anatase to rutile. The presence of N and F atoms in the lattice of TiO_2 is responsible for the visible light catalytic activity. In UV-Vis DRS tests, the spectrum of NFTO exhibited red shift compared with Degussa P25 and the band gap was reduced to around 2.92 eV. Under optimal calcination temperature and dopant concentration conditions, the NFTO photocatalyst exhibited the highest activity in the photodegradation reaction tests of 4-chlorophenol under visible light irradiation with a degradation rate of 75.84%. Besides, the 5-recycle test showed that NFTO photocatalyst could be reused and its activity kept stable under visible light irradiation.

Key words: TiO_2; N-F-codoping; photocatalyst; sol-gel process

DOI: 10.1016/S1001-0742(10)60656-0

Citation: Li X H, Zhang H D, Zheng X X, Yin Z Y, Wei L, 2011. Visible light responsive N-F-codoped TiO_2 photocatalysts for the degradation of 4-chlorophenol. Journal of Environmental Sciences, 23(11): 1919–1924

Introduction

In the past decades, nano-sized TiO_2 with distinguished advantages such as nontoxicity, low cost, chemical inertness, high decomposition and mineralization rate, has been widely studied and employed in photocatalytic decomposition of pollutants. TiO_2 is regarded as one of the most promising materials in environmental protection and solar energy conversion. However, conventional TiO_2 can be activated only by ultraviolet (UV) light irradiating due to the wide band gap energy (3.2 eV for anatase). This is a technological limitation when aiming at implementation of large scale sustainable technologies with renewable energy sources such as solar light, because UV light only accounts for 5% of solar energy compared to the visible region (45%) (Gole et al., 2004). The development of visible light responsive TiO_2 photocatalysts is greatly important for the large-scale application of TiO_2 photocatalysts.

Several efforts have been made to dope TiO_2 with various metals as well as nonmetals so as to make it photocatalytically active in visible light. Metal doping was limited for its negative effects on the thermal instability of doped TiO_2 catalysts, the increase of carrier-recombination centers (Choi et al., 1994) or the requirement of expensive ion-implantation apparatus (Anpo, 1997). To overcome the problem, doping TiO_2 with N had attracted considerable attention due to its photoactivity in the visible region. Furthermore, N-doped TiO_2 catalyst demonstrated similar photocatalytic activity to TiO_2 catalyst in UV range (Asahi et al., 2001). Since then, many nonmetal elements, including C (Irie et al., 2003), S (Ohno et al., 2004a) and F (Park and Choi, 2004), had been investigated in TiO_2 doping. Recently, nonmetal elements codoped TiO_2 catalysts, including C-S-codoped TiO_2 (Ohno et al., 2004b), S-N-codoped TiO_2 (Wei et al., 2008), F-N-codoped TiO_2 (Xie et al., 2007) and B-N-codoped TiO_2 (Gombac et al., 2007) have been prepared. Recent studies have revealed that codoping of TiO_2 could result in the development of additional visible active photocatalysts. Codoping of TiO_2 could exhibit significant photocatalytic improvement compared to mono-doping of TiO_2 due to the synergistic effect of nonmetal elements (Livraghi et al., 2009).

In this work, visible light responsive N-F-codoped TiO_2 (NFTO) photocatalysts were prepared by a simple

* Corresponding author. E-mail: xuxuzheng@ctbu.edu.cn

sol-gel process with tetrabutyl titanate ($Ti(OBu)_4$) and ammonium fluoride (NH_4F) as precursors. The effects of calcination temperature and preparation parameter on the structure and photocatalytic activity of catalysts under visible light irradiation were studied systematically. Furthermore, the application of NFTO photocatalysts in wastewater treatment processes for the degradation of environmental contaminants was investigated. The activity of NFTO was evaluated in the photocatalytic degradation of 4-chlorophenol under visible light irradiation.

1 Experimental

1.1 Materials

Tetrabutyl titanate (chemical pure grade, Sinopharm Chemical Reagent Co., Ltd., China), 4-chlorophenol (chemical pure grade, Sinopharm Chemical Reagent Co., Ltd., China), absolute alcohol and diethanolamine (analytical grade, Chongqing Chuandong Chemical Reagent Co., Ltd., China), ammonium fluoride (analytical grade, Chengdu Kelong Chemical Reagent Co., Ltd., China) were used as received. All solution was prepared by distilled water.

1.2 Catalyst preparation

NFTO catalysts were prepared by a sol-gel process. The mixture containing $Ti(OBu)_4$ (40 mL) and absolute alcohol (120 mL) was stirred for 30 min at 30°C, followed by the addition of diethanolamine. After another 30 min of stirring, solution A was obtained. NH_4F was dissolved in 6.4 mL distilled water. Then 40 mL absolute alcohol was added under stirring to produce solution B. Solution B was then dropwise added in solution A under vigorous stirring by a vermicular pump. After 2 hr of stirring, the solution obtained was aged at room temperature for 24 hr to form a sol. The sol was distilled by a rotary evaporator for reclaiming impregnant and the gel was then dried at 105°C. The NFTO catalysts were obtained by rubbing and calcinations of dry gel at certain temperatures for 3 hr. Before the final step of calcination, each sample was pretreated at 300°C for 1 hr and then heated to the certain temperatures with a rate of 2°C/min. Each NFTO catalyst was denoted as NFTO (n, T), where hereafter n represents the molar ratio of NH_4F to $Ti(OBu)_4$ and T represents calcination temperature. TiO_2 catalyst was prepared under the same conditions except no adding NH_4F and used as the reference sample.

1.3 Catalyst characterization

X-ray diffraction (XRD) measurements were performed on a Shimadzu XRD-6000 X-ray diffractometer with Cu $K\alpha$ (λ = 0.15406 nm) radiation from 10° to 70° in 2θ. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo VG MultiLab 2000 instrument using Al $K\alpha$ radiation ($h\nu$ = 1486.6 eV) as excitation source. The binding energies values were relatively corrected according to the C 1s signal at 284.6 eV. Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) were recorded on a Shimadzu UV-2550 UV-Vis spectrophotometer using $BaSO_4$ as reference.

1.4 Photocatalytic degradation of 4-chlorophenol

Photocatalytic activity of the prepared catalyst was measured by the photodegradation of 4-chlorophenol. The photocatalytic reaction was carried out on a multi-tube mixing photochemical reaction apparatus (Model XPA-7, Xujiang electromechanical Co., Ltd., China). A 500-W xenon lamp with a 400-nm cut-off filter was used as the visible light source. In a typical test, 40 mL of 4-chlorophenol aqueous solution with a concentration of 10 mg/L and catalyst were loaded in a 50 mL quartz cuvette and stirred using a magnetic stirrer of XPA-7. The amount of catalyst used was 2.0 g/L of 4-chlorophenol aqueous solution. The reaction mixture was stirred for 30 min in the dark to reach adsorption equilibrium. Then the air was accessed in each tube and turn on cooling water system and the xenon lamp. For certain interval, the reaction mixture was filtered using 0.20 μm membrane. The absorbency of the filtrate was determined by a Shanghai Techcomp UV-1102 UV-Vis spectrophotometer at 224 nm.

2 Results and discussion

2.1 XRD analysis

Figure 1 shows the XRD patterns of NFTO (0.1, T) catalysts and reference TiO_2 samples calcined at different temperatures. As indicated in Fig. 1, NFTO (0.1, 400°C) and TiO_2 (0, 400°C) give the patterns with only the peaks related to anatase phase. Rutile phase related peaks arise in the pattern of TiO_2 while calcination temperature increases to 500°C. For NFTO, when the calcination temperature is lower than 600°C, rutile phase related peaks can not be observed, implying that N-F-codoping inhibits the phase transition of TiO_2 from anatase to rutile. The possible reason for this fact was that F-doping inhibited the formation of rutile phase of TiO_2. Phase transition of TiO_2 from anatase to rutile was inhibited by the addition of Ti^{4+} complexing ions, such as phosphate, sulfate or fluoride (Izumi, 1978). F and Ti^{4+} could form ligand which

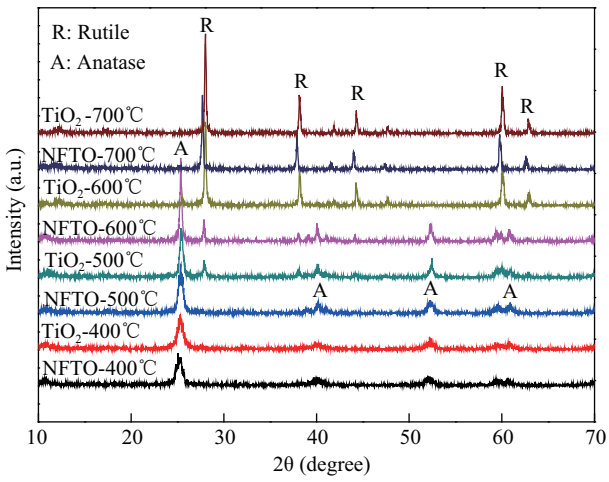

Fig. 1 XRD patterns of NFTO and TiO_2 calcined at different temperatures.

prevented the condensation of spiral chains of anatase TiO_6 octahedra to form linear chains of rutile TiO_6 octahedra but the growth of anatase spiral chains was still possible in this case (Li et al., 2005). Figure 1 also shows that the peak intensity of anatase increases and the width of the (101) diffraction peak of anatase phase becomes narrower with the increase of calcination temperature (from 400 to 500°C). This suggests that the particle size of catalyst increases from 400 to 500°C.

The weight fractions of anatase in anatase-rutile mixtures were calculated from the following equation (Spurr and Myers, 1957; Gandhe and Fernandes, 2005; Du et al., 2008):

$$X_A = (1 + \frac{I_R}{I_A K_2})^{-1} \quad (1)$$

where, X_A (%) is the weight fraction of anatase in the sample; I_R and I_A are obtained from the peak intensities of rutile (110) and anatase (101) diffractions, respectively; K_2 is a constant as 0.79.

The average particle size for the catalysts was calculated by Scherrer equation (Li et al., 2003):

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (2)$$

where, D (nm) is the average particle size of the sample, K is a constant of 0.89, λ is the wavelength characteristic of the Cu $K\alpha$ radiation, β is the full width at half maximum (in radians), and θ is the diffraction angle.

Table 1 presents the weight fractions of anatase in anatase-rutile mixtures with the average particle size for the catalysts in the temperature range of 400–700°C. We can see that the effect of calcination temperature on the crystal phase and particle size is significant. Higher calcination temperature results in the growth of rutile phase and produces catalysts with bigger particle size. The NFTO catalysts demonstrate smaller average particle size than TiO_2 samples with the same calcination temperature. Thus, a fine control of calcination temperature is crucial.

Table 1 Effect of calcination temperatures on crystal phase and average particle size of samples

Temperature (°C)	Sample	X_A (%)	Average particle size (nm)
400	NFTO	100	13.2
	TiO_2	100	13.6
500	NFTO	100	15.6
	TiO_2	81.32	18.5
600	NFTO	80.83	30.8
	TiO_2	5.49	36.5
700	NFTO	4.90	43.4
	TiO_2	0	44.1

X_A: weight fraction of anatase in the sample.

2.2 XPS analysis

Figure 2 gives the XPS spectra of NFTO (0.1, 600°C). The XPS curves were fitted by Gaussian-Lorentzian curves (Beamson and Briggs, 1992). The core level of Ti 2p shows two peaks centered at 458.4 and 464.1 eV, respectively. A split of 5.7 eV between the doublets indicates that Ti exists mostly in the form of Ti^{4+} (Reddy et al., 2006; Xie et al., 2008). The O 1s spectrum demonstrates a strong peak centered at 529.7 eV which can be attributed to lattice oxygen of TiO_2. The shoulder centered at 532.0 eV

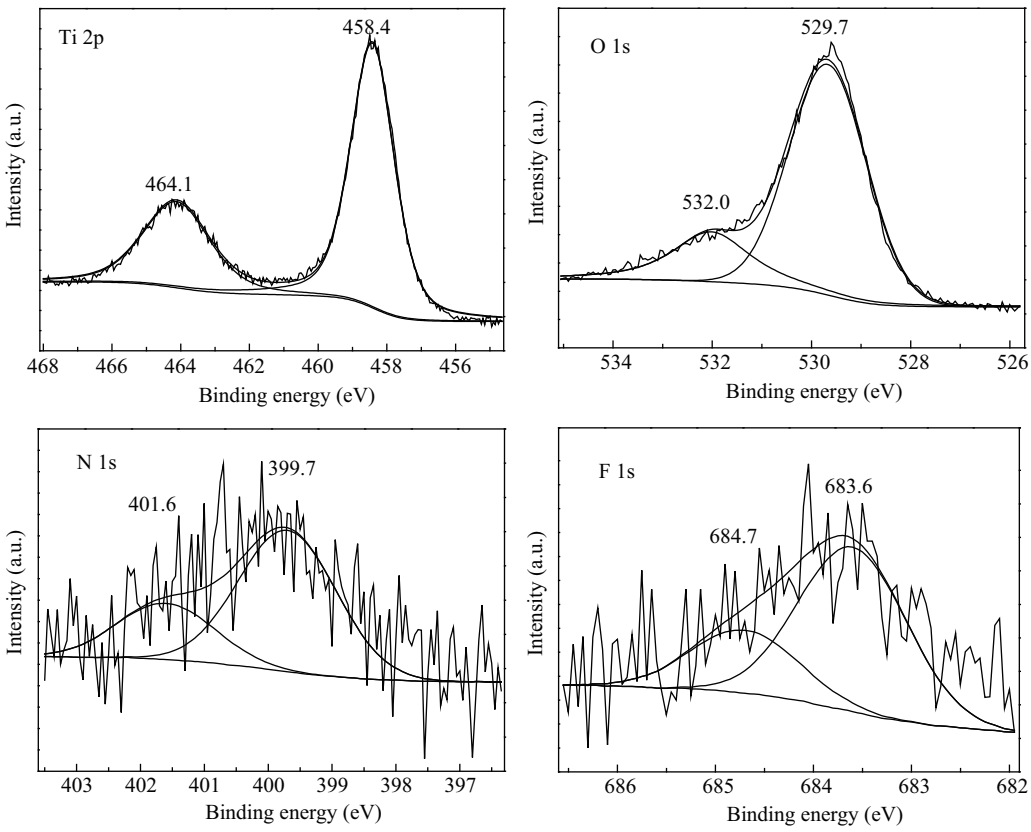

Fig. 2 XPS spectra of NFTO (0.1, 600°C).

is assigned to the contributions from surface hydroxides (Erdem et al., 2001).

In the N 1s spectrum, the peak centered at 399.7 eV is assigned to the N–Ti–O linkage in TiO_2 lattice and responsible for the enhanced visible light activity (Jang et al., 2006; Pelaez et al., 2009). The N 1s binding energy of TiN is 397.3 eV but the N 1s binding energy of NFTO (0.1, 600°C) is 2.4 eV higher. The possible reason is that the oxygen in TiO_2 lattice is substituted by N and the N–Ti–O bond is thus formed. Higher electronegativity of O than N makes the electron cloud density of N in the N–Ti–O structure lower than that of the N–Ti–N bond in TiN and subsequently the electronic binding energy of N in N–Ti–O bond increases. N 1s spectrum also demonstrates a peak centered at 401.6 eV reflecting the existence of nitrogen containing chemisorbed compounds like NO*x* (Su et al., 2008). The total content of N in sample is 0.92 at.% calculated from XPS survey spectra.

The F 1s spectrum gives two peaks centered at 683.6 and 684.7 eV, respectively. The peak centered at 683.6 eV is assigned to oxyfluoride. The peak centered at 684.7 eV is attributed to the F–Ti–O linkage in TiO_2 lattice (Im et al., 2009). The atom radius of F is similar to that of O. The replacement of the O atoms connected directly to Ti atom in TiO_2 lattice by F atoms is relatively easy and thus induces the photocatalytic activity of NFTO catalysts in visible region. The total content of F in the sample is determined to be 0.56 at.% according to the XPS survey spectra. Further study and mechanistic understanding is under investigation.

2.3 UV-Vis analysis

Figure 3 shows the UV-Vis DRS spectra of Degussa P25 and NFTO (0.1, 600°C), respectively. The spectrum of NFTO demonstrates a red shift and higher visible light absorption compared with Degussa P25, suggesting that NFTO is a photocatalyst driven by visible light. The band gap of the samples was determined by the following equation (O'Regan and Grätzel, 1991):

$$E_g = 1239.8/\lambda \quad (3)$$

where, E_g (eV) is the band gap and λ (nm) is the wavelength of the absorption edge in the spectrum. The absorption edge of the NFTO occurred at around 424 nm and the band gap was changed to about 2.92 eV, indicating that N-F-codoping could be a promising approach for increasing the visible light photocatalytic activity.

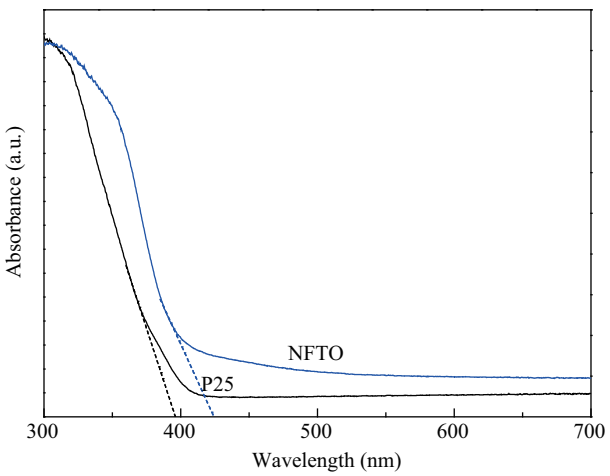

Fig. 3 UV-Vis DRS spectra of P25 and NFTO (0.1, 600°C).

2.4 Photocatalytic activity for the degradation of 4-chlorophenol

2.4.1 Effect of calcination temperature on photocatalytic activity

Figure 4 gives the results of photocatalytic degradation of 4-chlorophenol catalyzed by NFTO (0.01, *T*) under visible light irradiation for 5 hr. Among the NFTO catalysts, the photocatalytic activity increases with the increase of calcination temperature from 400 to 600°C. At 600°C, the catalyst reaches the highest activity. This should mainly result from the fact that NFTO (0.01, 600°C) was of anatase-rutile mixed phase and small nano-sized particle. In mixed phase of TiO_2, the electron transfer from rutile to anatase can effectively inhibit electron–hole (e^-–h^+) recombination (Bickley et al., 1991; Shi and Weng, 2008), thus enhancing the photocatalytic efficiency. Meanwhile, with calcination temperature further increasing, rutile content as well as particle size of NFTO catalyst increases and its photocatalytic activity decreases. The results show that the phase composition, anatase content and particle size of NFTO photocatalyst are important factors in high photocatalytic activity.

2.4.2 Effect of dopant concentration on photocatalytic activity

Figure 5 presents the results of photocatalytic degradation of 4-chlorophenol catalyzed by NFTO (*n*, 600°C) under visible light irradiation for 5 hr. We can see that NFTO (0.1, 600°C) shows the highest photocatalytic activity. According to doping theory (Choi et al., 1994; Suda et al., 2004), an optimal dopant concentration is critical for the NFTO catalysts. At the dopant concentration below the optimal value, photocatalytic activity increases with increasing dopant concentration due to more available trapping sites inhibiting electron–hole pair recombination. When the dopant concentration is higher than the optimal

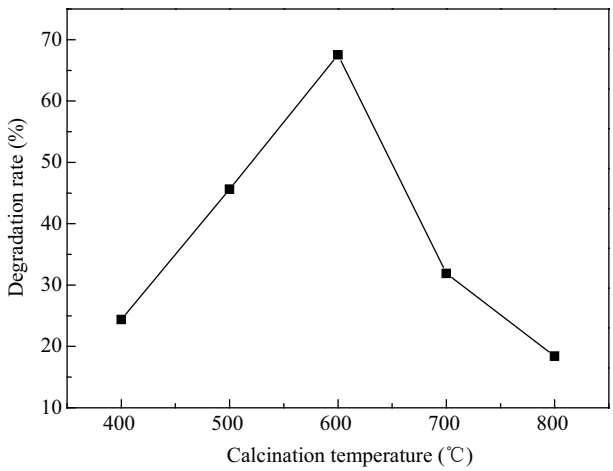

Fig. 4 Effect of calcination temperature on photocatalytic activity under visible light.

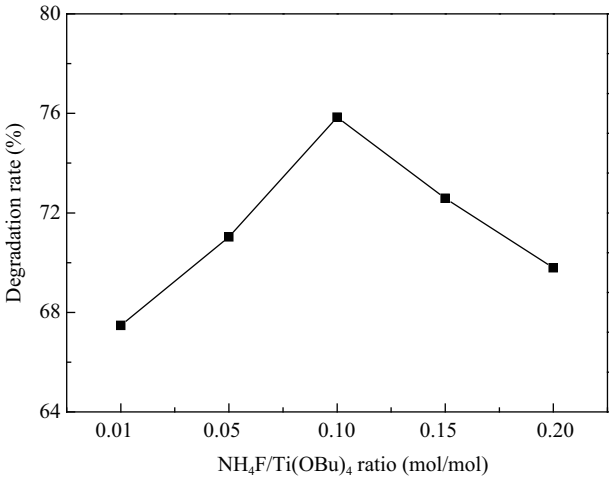

Fig. 5 Effect of molar ratio of NH_4F to $Ti(OBu)_4$ on photocatalytic activity under visible light.

value, the electron–hole pair recombination rate exponentially increases because the average distance between two trap sites decreases with increasing number of dopants.

2.4.3 Photocatalytic reaction results

Figure 6 shows the photocatalytic activities of NFTO (0.1, 600°C) and TiO_2 (0, 600°C) catalysts in the degradation 4-chlorophenol under visible light irradiation for 5 hr. A blank run without any catalyst was taken as the comparison. The results showed that NFTO catalyst exhibits high photoactivity under visible light with a degradation rate of 75.84%. The adsorption of 4-chlorophenol on TiO_2 surface may make such small change compared to a blank run. N-doped TiO_2 catalyst could give 54.62% degradation rate of 4-chlorophenol under visible light irradiation for 5 hr in previous report (Yu et al., 2007). Thus, NFTO (0.1, 600°C) photocatalyst shows high degradation rate and higher catalytic activity than N-doped catalyst under visible light irradiation.

2.4.4 Reuse of catalyst

The repeated tests were carried out to evaluate the stability of NFTO (0.1, 600°C) catalyst. The degradation rate of 4-chlorophenol at 72.48% was achieved under visible light irradiation for 5 hr after the fifth recycle, as shown in Fig. 7. The results show that the NFTO (0.1, 600°C) catalyst is stable and a promising material in environmental remediation.

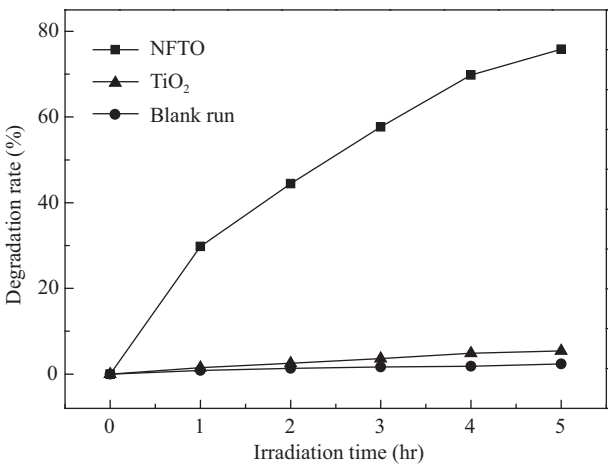

Fig. 6 Photocatalytic activity of NFTO and TiO_2 in the photodegradation of 4-chlorophenol and blank run under visible light.

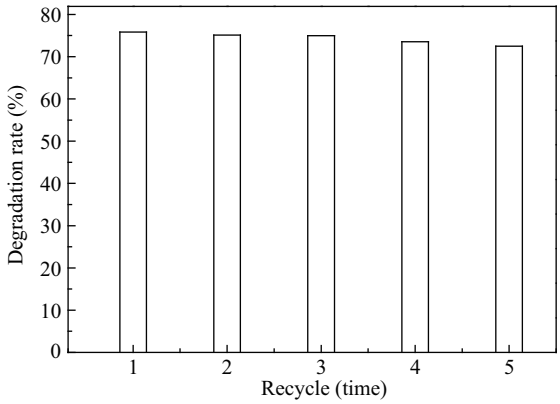

Fig. 7 Photocatalytic activity of NFTO (0.1, 600°C) catalyst in the degradation of 4-chlorophenol in five recycles under visible light.

3 Conclusions

In this research, the NFTO photocatalysts were prepared, characterized and used in the photocatalytic degradation of 4-chlorophenol under visible light irradiation. The result indicated that N-F-codoping inhibited the phase transition of TiO_2 from anatase to rutile. In addition, the presence of N and F atoms in the lattice of TiO_2 is responsible for the visible light catalytic activity due to the band gap narrowing to around 2.92 eV. Further, the calcination temperature and dopant concentration have significant effects on the crystal phase composition, the particle size and the photocatalytic activity of the formed NFTO catalyst. Systematical investigation showed that the NFTO catalyst prepared at calcination temperature of 600°C and molar ratio (NH_4F to $Ti(OBu)_4$) of 0.1 exhibited the highest photocatalytic activity under visible light irradiation. A degradation rate of 75.84% for 4-chlorophenol can be achieved in 5 hr. Besides, the NFTO photocatalyst can be recycled with stable photocatalytic activity in at least 5 recycles and thus regarded as a promising material in environmental remediation.

Acknowledgments

This work was financially supported by the Science and Technology Project of Education Commission of Chongqing of China (No. KJ110709), the Key Science Project of Ministry of Education of China (No. 2008119), the Colleges and Universities Innovation Team Project of Chongqing of China (No. KJTD201020) and the Science and Technology Project of Engineering Research Centre for Waste Oil, Ministry of Education of China (No. FYKJ2009012).

References

Anpo M, 1997. Photocatalysis on titanium oxide catalysts approaches in achieving highly efficient reactions and real-

izing the use of visible light. *Catalysis Surveys from Japan*, 1(2): 169–179.

Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y, 2001. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science*, 293(5528): 269–271.

Beamson G, Briggs D, 1992. High resolution monochromated X-ray photoelectron spectroscopy of organic polymers: A comparison between solid state data for organic polymers and gas phase data for small molecules. *Molecular Physics*, 76(4): 919–936.

Bickley R I, Gonzalez-carreno T, Lees J S, Palmisano L, Tilley R J D, 1991. A structural investigation of titanium dioxide photocatalysts. *Journal of Solid State Chemistry*, 92(1): 178–190.

Choi W, Termin A, Hoffmann M R, 1994. The role of metal ion dopants in quantum-sized TiO_2: correlation between photoreactivity and charge carrier recombination dynamics. *The Journal of Physical Chemistry B*, 98(51): 13669–13679.

Du P, Bueno-lópez A, Verbaas M, Almeida A R, Makkee M, Moulijn J A et al., 2008. The effect of surface OH-population on the photocatalytic activity of rare earth-doped P25-TiO_2 in methylene blue degradation. *Journal of Catalysis*, 260(1): 75–80.

Erdem B, Hunsicker R A, Simmons G W, Sudol E D, Dimonie V L, Ei-aasser M S, 2001. XPS and FTIR surface characterization of TiO_2 particles used in polymer encapsulation. *Langmuir*, 17(9): 2664–2669.

Gandhe A R, Fernandes J B, 2005. A simple method to synthesize N-doped rutile titania with enhanced photocatalytic activity in sunlight. *Journal of Solid State Chemistry*, 178(9): 2953–2957.

Gole J L, Stout J D, Burda C, Lou Y B, Chen X B, 2004. Highly efficient formation of visible light tunable $TiO_{2-x}N_x$ photocatalysts and their transformation at the nanoscale. *The Journal of Physical Chemistry B*, 108(4): 1230–1240.

Gombac V, De Rogatis L, Gasparotto A, Vicario G, Montini T, Barreca D et al., 2007. TiO_2 nanopowders doped with boron and nitrogen for photocatalytic applications. *Chemical Physics*, 339(1-3): 111–123.

Im J S, Yun S M, Lee Y S, 2009. Investigation of multielemental catalysts based on decreasing the band gap of titania for enhanced visible light photocatalysis. *Journal of Colloid and Interface Science*, 336(1): 183–188.

Irie H, Watanabe Y, Hashimoto K, 2003. Carbon-doped anatase TiO_2 powders as a visible-light sensitive photocatalyst. *Chemistry Letters*, 32(8): 772–773.

Izumi F, 1978. The polymorphic crystallization of titanium(IV) oxide under hydro-thermal conditions. II. the roles of inorganic anions in the nucleation of rutile and anatase from acid solutions. *Bulletin of the Chemical Society of Japan*, 51(6): 1771–1776.

Jang J S, Kim H G, Ji S M, Bae S W, Jung J H, Shon B H et al., 2006. Formation of crystalline $TiO_{2-x}N_x$ and its photocatalytic activity. *Journal of Solid State Chemistry*, 179(4): 1067–1075.

Li D, Haneda H, Labhsetwar N K, Hishita S, Ohashi N, 2005. Visible-light-driven photocatalysis on fluorine-doped TiO_2 powders by the creation of surface oxygen vacancies. *Chemical Physics Letters*, 401(4-6): 579–584.

Li X Z, Liu H, Cheng L F, Tong H J, 2003. Photocatalytic oxidation using a new catalyst-TiO_2 microsphere-for water and wastewater treatment. *Environmental Science & Technology*, 37(17): 3989–3994.

Livraghi S, Elghniji K, Czoska A M, Paganini M C, Giamello E, Ksibi M, 2009. Nitrogen-doped and nitrogen–fluorine-codoped titanium dioxide. Nature and concentration of the photoactive species and their role in determining the photocatalytic activity under visible light. *Journal of Photochemistry and Photobiology A: Chemistry*, 205(2-3): 93–97.

Ohno T, Akiyoshi M, Umebayashi T, Asai K, Mitsui T, Matsumura M, 2004a. Preparation of S-doped TiO_2 photocatalysts and their photocatalytic activities under visible light. *Applied Catalysis A: General*, 265(1): 115–121.

Ohno T, Tsubota T, Toyofuku M, Inaba R, 2004b. Photocatalytic activity of a TiO_2 photocatalyst doped with C^{4+} and S^{4+} ions having a rutile phase under visible light. *Catalysis Letters*, 98(4): 255–258.

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

Park H, Choi W, 2004. Effects of TiO_2 surface fluorination on photocatalytic reactions and photoelectrochemical behaviors. *The Journal of Physical Chemistry B*, 108(13): 4086–4093.

Pelaez M, de la Cruz A A, Stathatos E, Falaras P, Dionysiou D D, 2009. Visible light-activated N-F-codoped TiO_2 nanoparticles for the photocatalytic degradation of microcystin-LR in water. *Catalysis Today*, 144 (1-2): 19–25.

Reddy B M, Rao K N, Reddy G K, Bharali P, 2006. Characterization and catalytic activity of V_2O_5/Al_2O_3-TiO_2 for selective oxidation of 4-methylanisole. *Journal of Molecular Catalysis A: Chemical*, 253 (1-2): 44–51.

Shi L, Weng D, 2008. Highly active mixed-phase TiO_2 photocatalysts fabricated at low temperature and the correlation between phase composition and photocatalytic activity. *Journal of Environmental Sciences*, 20(10): 1263–1267.

Spurr R A, Myers H, 1957. Quantitative analysis of anatase-rutile mixtures with an X-ray diffractometer. *Analytical Chemistry*, 29(5): 760–762.

Suda Y, Kawasaki H, Ueda T, Ohshima T, 2004. Preparation of high quality nitrogen doped TiO_2 thin film as a photocatalyst using a pulsed laser deposition method. *Thin Solid Films*, 453-454: 162–166.

Su Y L, Zhang X W, Zhou M H, Han S, Lei L C, 2008. Preparation of high efficient photoelectrode of N-F-codoped TiO_2 nanotubes. *Journal of Photochemistry and Photobiology A: Chemistry*, 194(2-3): 152–160.

Wei F Y, Ni L S, Cui P, 2008. Preparation and characterization of N-S-codoped TiO_2 photocatalyst and its photocatalytic activity. *Journal of Hazardous Materials*, 156(1-3): 135–140.

Xie Y, Li Y Z, Zhao X J, 2007. Low-temperature preparation and visible-light-induced catalytic activity of anatase F-N-codoped TiO_2. *Journal of Molecular Catalysis A: Chemical*, 277(1-2): 119–126.

Xie Y, Zhao X J, Li Y Z, Zhao Q N, Zhou X D, Yuan Q H, 2008. CTAB-assisted synthesis of mesoporous F-N-codoped TiO_2 powders with high visible-light-driven catalytic activity and adsorption capacity. *Journal of Solid State Chemistry*, 181(8): 1936–1942.

Yu H, Zheng X X, Yin Z Y, Tao F, Fang B B, Hou K S, 2007. Preparation of nitrogen-doped TiO_2 nanoparticle catalyst and its catalytic activity under visible light. *Chinese Journal of Chemical Engineering*, 15(6): 802–807.