

Nitrogen Doped Titania Plates with Dominant {001} Facets: The Effect of Surface Fluorination on Visible-Light Photocatalytic Activity

Jian-Wen Shi^{1,a}, Chong Xie^{1,b}, Guodong Li^{2,c} and Chunming Niu^{1,d}

¹Center of Nanomaterials for Renewable Energy, State Key Laboratory of Electrical Insulation and Power Equipment, School of Electrical Engineering, Xi'an Jiaotong University, Xi'an 710049, China.

²State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

^ashijwn@163.com, ^bxiechong@stu.xjtu.edu.cn, ^clgd@jlu.edu.cn, ^dcniu@mail.xjtu.edu.cn

Keywords: Photocatalysis; TiO₂; Doping; {001} facet; Visible light.

Abstract. In order to investigate the effect of surface fluorination, nitrogen doped titania plates with dominant {001} facets (abbr. NTP) were prepared by one-pot hydrothermal method in the presence of HF, and then two commonly used methods, calcination treatment and NaOH washing were carried out to get rid of F ions anchored on the surface of NTP. The obtained samples were characterized by XRD, SEM and XPS in detail, and their photocatalytic activities were evaluated by the photocatalytic discoloration of methylene blue and methyl orange under visible light irradiation. The results showed that surface fluorination presented positive effect on the visible-light photocatalytic activity of NTP. The reason could be attributed to the fact that the fluorinated surface was helpful for the generation of •OH radicals.

Introduction

The photocatalytic degradation of organic pollutants by semiconductor catalysts, such as TiO₂, has been extensively investigated in the past decades [1]. Owing to the high photocatalytic activity and the ability to utilize visible light, nonmetal doped TiO₂ crystals (e.g. N, C, S, F) with exposed {001} facets have attracted considerable attention in the recent years [2-5]. In our recent work [6], we successfully prepared N-doped anatase TiO₂ plates with dominated {001} facets (abbr. NTP) by one-pot hydrothermal method in the presence of HF, and the obtained samples (S10, S20 and S30) presented photocatalytic activity for the discoloration of methylene blue (MB) under visible light irradiation. XPS disclosed that lots of F ions were anchored on the surface of these samples due to the addition of HF used as facet controlling reagent. Recently, some publications reported that clean TiO₂ plates (surface-fluorine has been cleaned) displayed higher photocatalytic activity in comparison with fluorine-capped TiO₂ [7]. Is the effect of surface-fluorine on photocatalytic activity of TiO₂ plates positive or negative? In order to answer this question, in current work, we applied two commonly used methods, calcination treatment and NaOH washing, to get rid of F ions anchored on the surface of NTP, and then compared their photocatalytic activities under visible light irradiation.

Experimental Section

Calcination Treatment. Nitrogen doped titania plates with dominant {001} facets, marked as S10, S20 and S30, were prepared according to the same procedure described in our previous paper [6]. In order to investigate the effects of surface fluorination, the above samples were calcined at 600 °C in air for 2 h at a heating rate of 5 °C min⁻¹ to get rid of F ions anchored on the surface of samples, and the resulting samples were labeled as S10-air, S20-air and S30-air, respectively.

NaOH Washing. In order to remove the surface-fluorine ions, the samples, S10, S20 and S30 were washed with NaOH solution according to the procedure: the as-prepared sample was dispersed in 20 mL of 10 M NaOH aqueous solution under vigorous stirring for 30 min in an ultrasonic cleaner. Then, the sample was centrifuged and washed five times with deionized water, and then was dried overnight

at 80 °C in air. The obtained samples were labeled as S10-NaOH, S20-NaOH and S30-NaOH, respectively.

Characterizations. X-ray diffraction (XRD) patterns were recorded at room temperature with an X' pert PROMPD diffractometer (PANalytical, Holland) with copper $K_{\alpha 1}$ radiation. Scanning electron microscopy (SEM) images were obtained by an S-4800 (Hitachi, Japan) equipment. X-ray photoelectron spectroscopy (XPS) analyses were tested on an ESCALAB250 (Thermo Scientific, America) with aluminum K_{α} radiation.

Experimental Procedures of Photocatalytic Decoloration. The photocatalytic experiment was carried out in a photo reaction system (as illustrated in our previous publication [8]) by using MB as a model pollutant. A 1000 W Xe lamp equipped with a 420 nm cut-off glass filter (removing the UV irradiation below 420 nm wavelength), positioned in the center of a water-cooled quartz jacket, was used to offer visible light irradiation. At the side of quartz jacket, a 50-mL cylindrical vessel was used as the reactive bottle to load reaction solution. The distance between lamp and reactive bottle was 40 mm. In the bottom of the reactive bottle, a magnetic stirrer was equipped to achieve effective dispersion. Photocatalyst powder (50 mg) was added into 50 mL of 10 mg/L MB solution to form suspension. Then, the suspension was irradiated with visible light. During the irradiation, the suspension was stirred continuously. At given time interval, 3 mL of suspension was taken out and immediately centrifuged to eliminate the solid particles. The absorbance of the filtrate was measured by a spectrophotometer at the maximum absorbance peak 665 nm.

Results

XRD Analysis. Fig. 1 shows the XRD patterns of all samples. Compared with S10, a new crystal phase, rutile TiO_2 , appears in S10-air. TiN decreased to about 20% in S10-air from 81% in S10, and anatase TiO_2 increased to about 50% in S10-air from 19% in S10, respectively, implying some parts of TiN were transformed into rutile TiO_2 and anatase TiO_2 in the process of calcination. Compared with S20, a new and minor peak appeared at $2\theta = 23.40^\circ$ in the XRD pattern of S20-air, which is corresponding to (100) plane of cubic titanium oxide fluoride ($TiOF_2$) (Ref. No 01-077-0132), indicating S20-air is composed of four crystal phases, major anatase TiO_2 (88%), rutile TiO_2 (4%), TiN (5%) and a little of $TiOF_2$ (3%). For S30-air, only two kinds of phases were detected, anatase TiO_2 (96%) and $TiOF_2$ (4%).

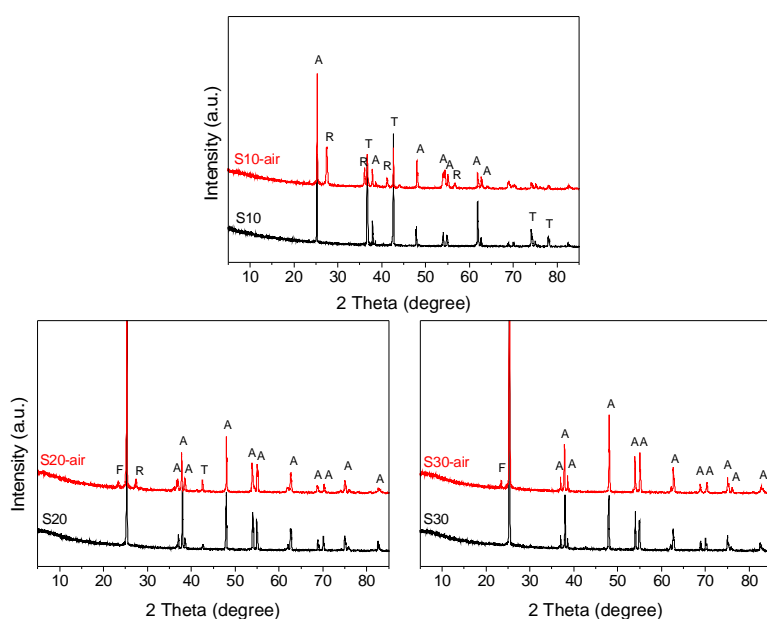


Fig. 1 The XRD patterns of samples (A: anatase; R: rutile; T: TiN; F: $TiOF_2$)

SEM. Compared with the morphologies of those samples before heat-treatment (see Fig. 3 in our previous paper [6]), the morphologies of these samples were changed greatly due to the calcination at 600 °C in air for 2 h (Fig. 2). As shown in Fig. 2a, some TiO₂ plates with dominant {001} facets appeared in S10-air, and these TiO₂ plates looked like to be embedded in the irregular bulks. Compared with the morphology of S20 (Fig. 3c in our previous paper [6]), calcination did not produced significant impact on its morphology (Fig. 2b) except for the fact that many regular rectangle pores generated on the surfaces, especially on the {001} facets (the inset in Fig. 2b), which should be attributed to the escape of F and N during the calcination process [9]. Similarly, the calcination did not arouse obvious influence on the morphology of TiO₂ plates in S30-air (Fig. 2c). Similarly, many regular rectangle pores also appeared on the surfaces, especially on the {001} facets of S30-air (the inset in Fig. 2c).

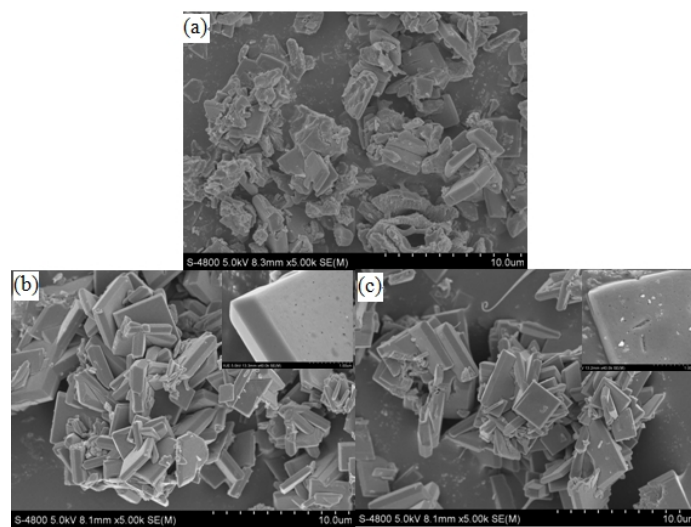


Fig. 2 SEM images of samples: (a) S10-air; (b) S20-air; (c) S30-air

XPS Analysis. As a typical sample, S20-air was tested by XPS analysis. Compared with S20, the F1s peak disappeared in the XPS pattern of S20-air (Fig. 3), indicating calcination can get rid of F ions anchored on the surface of S20. Additionally, the intensity of N1s peak centered at 408.3 eV was weakened, implying some N ions have escaped during the calcination process.

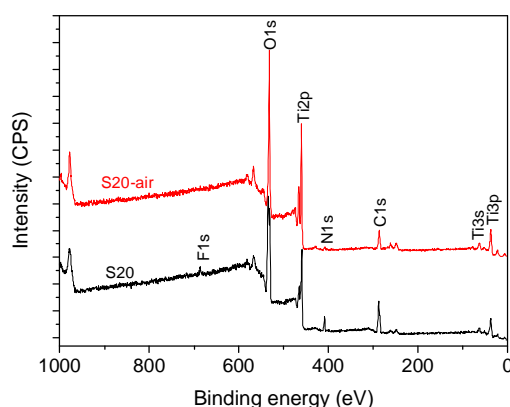


Fig. 3 The overall XPS spectra of S20 and S20-air.

Photocatalytic Activity. The photocatalytic activities of samples were evaluated by the decoloration of MB solution without investigating the degradation intermediates in detail. As shown in Fig. 4, calcination did not bring significant impact on the photocatalytic activity of S10. However, for S20 and S30, calcination had a negative impact on their photocatalytic activity.

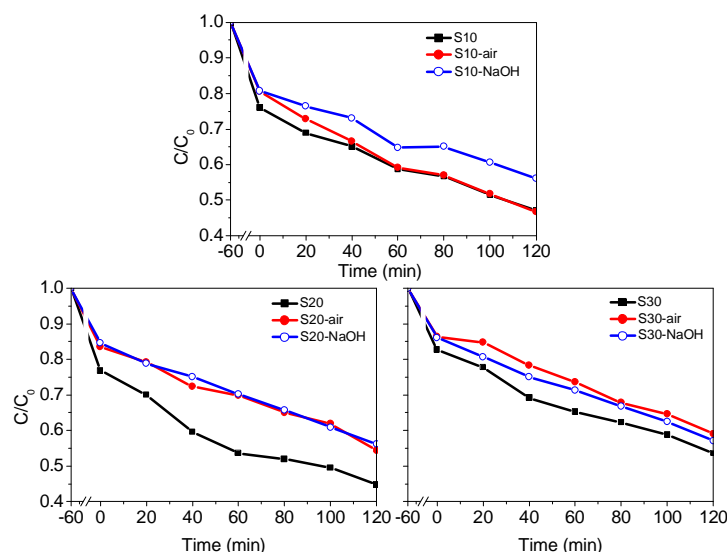


Fig. 4 Photocatalytic decoloration of MB solution over different photocatalysts under visible light irradiation ($\lambda > 420$ nm).

The Amount of Hydroxyl Radicals. Hydroxyl radical is a very important species produced in the process of photocatalysis, which is responsible for the decomposition of organic pollutant. In order to test the effect of hydrothermal treatment and following calcination on the generated amount of $\bullet\text{OH}$ radicals, the amount of $\bullet\text{OH}$ generated during photocatalysis of sample S20 and S20-air were measured according to the literature [3]. As shown in Fig. 5a, S20 produced more $\bullet\text{OH}$ radicals than S20-air.

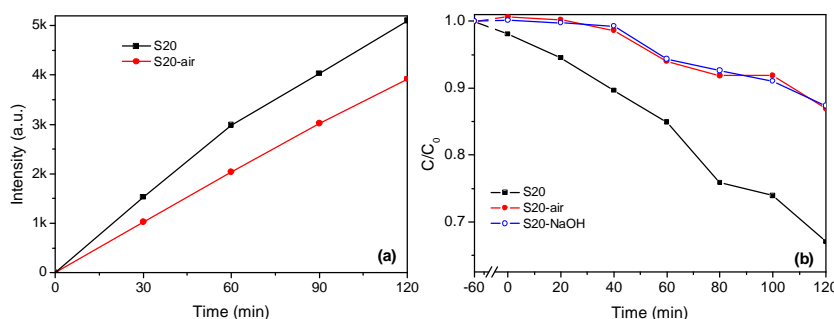


Fig. 5 (a) Comparison of the fluorescence signal intensities at 423 nm of S20 and S20-air; (b) Photocatalytic decoloration of MO solution over S20, S20-air and S20-NaOH under visible light irradiation ($\lambda > 420$ nm).

Discussion

It is well known that surface-fluorine can be removed from TiO_2 by calcining at 600°C in a static air atmosphere for 2 h [7,10]. Pan and co-workers thought the photocatalytic activity of TiO_2 with surface-fluorine or without surface-fluorine was closely associated with the property of reactants used as indicator [9]. The presence of surface-fluorine could enhance the adsorption of cationic reactant via the electrostatic-adsorption mode, but was unfavorable for the adsorption of anionic reactants [9]. MB is cationic reactant, so fluorine-capped TiO_2 can adsorb more MB molecules in comparison with clean TiO_2 , which cause its higher photocatalytic activity. In order to test whether this opinion is applicable in our work, an anionic reactant, methyl orange (MO) was used as indicator to distinguish the photocatalytic activities between clean TiO_2 plates and fluorine-capped TiO_2 plates, and the results are displayed in Fig. 5b. It can be seen that fluorine-capped TiO_2 plates, which should be lower

photocatalytic activity according to this opinion, possessed higher photocatalytic activity than clean TiO₂ plates. Therefore, this opinion is not suitable for our current work.

Maybe, other changes resulted from calcination, except for the removal of surface-fluorine dominated the photocatalytic activity of NTP samples. In order to clear the doubt, samples (S10, S20 and S30) washed by NaOH solution were used as photocatalysts to decolor MB solution in the same conditions. As confirmed by previous publication [11], NaOH washing procedure can not arouse other effects on the microstructure and property of samples except for the removal of surface-fluorine ions. A same rule was disclosed that clean TiO₂ plates displayed worse photocatalytic activity in comparison with corresponding fluorine-capped TiO₂ plates (Fig. 4). Therefore, it can be deduced surface fluorination is helpful to improve the photocatalytic activity of NTP in our experimental conditions.

In fact, as a novel method of surface modification, surface fluorination of TiO₂ has been intensively investigated in recent years [12-17], and lots of results have demonstrated that surface fluorination has positive effect on the enhancement of photocatalytic activity of TiO₂. For example, Minero and co-workers reported that surface fluorination of TiO₂ could improve the photocatalytic oxidation rate of phenol in aqueous solution [12]. Park and Choi found that surface-fluorinated TiO₂ showed enhanced photocatalytic activity in aqueous suspensions for the photocatalytic oxidation of Acid Orange 7 and phenol, and they proposed that the fluorinated surface favored the generation of •OH radicals, which were responsible for the enhanced oxidation [13]. Mrowetz and Selli demonstrated that more •OH radicals generated on fluorinated TiO₂ [14]. Park and Choi recently found that fluorinated TiO₂ can enhance the remote photocatalytic oxidation at the air/catalyst interface by facilitating the desorption of •OH radicals under UV irradiation [15]. Yu and co-workers' opinion is that surface-capping F ions on TiO₂ can reduce the recombination of photogenerated electrons and holes, enhance the formation of •OH radicals and finally improve the photocatalytic oxidation of some organics, because of its strong electron withdrawing ability [16,17]. From these previous reports, it can be inferred that the effect of surface fluorination of TiO₂ could be either positive or negative depending on the kind of substrate and experimental conditions [16]. In our present work, the effect of surface fluorination on the photocatalytic activity of NTP is positive, which can be ascribed to the fact that the fluorinated surface favors the generation of •OH radicals, as proved in Fig. 5a.

Conclusions

Calcination presented important effect on the microstructure and photocatalytic activity of NTP. Owing to calcination, many regular rectangle pores generated on the surfaces, especially on the {001} facets of NTP, some portions of TiN were transformed into rutile and anatase TiO₂, and a new crystal TiOF₂ formed in the structure of NTP. Surface fluorination played a positive role in the improvement of the photocatalytic activity of NTP for the decoloration of whether cationic reactant (MB) or anionic reactant (MO) because the fluorinated surface favored the generation of •OH radicals.

Acknowledgement

This work was sponsored by the Fundamental Research Funds for the Central Universities (2015gjh06), the National Natural Science Foundation of China (21371070), and the Opening Project of State Key Laboratory of Inorganic Synthesis and Preparative Chemistry (2015-14).

References

- [1] U. I. Gaya, A. H. Abdullah, Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems, *J. Photochem. Photobio. C: Photochem. Rev.* 9 (2008) 1-12.

- [2] G. Liu, H. G. Yang, X. Wang, L. Cheng, J. Pan, G. Q. Lu, H.-M. Cheng, visible light responsive nitrogen doped anatase TiO₂ sheets with dominant {001} facets derived from TiN, *J. Am. Chem. Soc.* 2009, 131, 12868-12869.
- [3] J.-W. Shi, C. Liu, C. He, J. Li, C. Xie, S. Yang, J.-W. Chen, S. Li, C. Niu, Carbon-doped titania nanoplates with exposed {001} facets: facile synthesis, characterization and visible-light photocatalytic performance, *RSC Adv.* 5 (2015) 17667-17675.
- [4] G. Liu, C. Sun, S. C. Smith, L. Wang, G. Q. M. Lu, H. M. Cheng, Sulfur doped anatase TiO₂ single crystals with a high percentage of {001} facets, *J. Colloid Interface Sci.* 349 (2010) 477-483.
- [5] X. Zong, Z. Xing, H. Yu, Z. Chen, F. Tang, J. Zou, G. Q. Lu, L. Wang, Photocatalytic water oxidation on F, N co-doped TiO₂ with dominant exposed {001} facets under visible light, *Chem. Commun.* 47 (2011) 11742-11744.
- [6] J.-W. Shi, H.-Y. Ai, J.-W. Chen, H.-J. Cui, S. Yang, S. Li, M.-L. Fu, Nitrogen doped titania plates with dominant {001} facets: Microstructure and property evolution, and their photocatalytic activities, *J. Mol. Catal. A* 395 (2014) 420-427.
- [7] J. Pan, G. Liu, G. Q. Lu, H.-M. Cheng, On the true photoreactivity order of {001}, {010}, and {101} facets of anatase TiO₂ crystals, *Angew. Chem. Int. Ed.* 50 (2011) 2133-2137.
- [8] J.-W. Shi, X. Zong, X. Wu, H.-J. Cui, B. Xu, L. Wang, M.-L. Fu, Carbon-doped titania hollow spheres with tunable hierarchical macroporous channel and enhanced visible light-induced photocatalytic activity, *ChemCatChem* 4 (2012) 488-491.
- [9] L. Pan, J.-J. Zou, S. Wang, X.-Y. Liu, X. Zhang, L. Wang, Morphology evolution of TiO₂ facets and vital influences on photocatalytic activity, *ACS Appl. Mater. Interfaces* 4 (2012) 1650-1655.
- [10] H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng, G. Q. Lu, Anatase TiO₂ single crystals with a large percentage of reactive facets, *Nature* 453 (2008) 638-641.
- [11] T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto, S. Sugihara, Visible-light-active titanium oxide photocatalyst realized by an oxygen-deficient structure and by nitrogen doping, *Appl. Catal. B* 42 (2003) 403-409.
- [12] C. Minero, G. Mariella, V. Maurino, E. Pelizzetti, Photocatalytic transformation of organic compounds in the presence of inorganic anions. 1. Hydroxyl-mediated and direct electron-transfer reactions of phenol on a titanium dioxide-fluoride system, *Langmuir* 16 (2000) 2632-2641.
- [13] H. Park, W. Choi, Effects of TiO₂ surface fluorination on photocatalytic reactions and photoelectrochemical behaviors, *J. Phys. Chem. B* 108 (2004) 4086-4093.
- [14] M. Mrowetz, E. Selli, Enhanced photocatalytic formation of hydroxyl radicals on fluorinated TiO₂, *Phys. Chem. Chem. Phys.* 7 (2005) 1100-1102.
- [15] J. S. Park, W. Y. Choi, Enhanced remote photocatalytic oxidation on surface-fluorinated TiO₂, *Langmuir* 20 (2004) 11523-11527.
- [16] J. Yu, W. Wang, B. Cheng, B.-L. Su, Enhancement of photocatalytic activity of mesoporous TiO₂ powders by hydrothermal surface fluorination treatment, *J. Phys. Chem. C* 113 (2009) 6743-6750.
- [17] Q. Xiang, K. Lv, J. Yu, Pivotal role of fluorine in enhanced photocatalytic activity of anatase TiO₂ nanosheets with dominant (001) facets for the photocatalytic degradation of acetone in air, *Appl. Catal. B* 96 (2010) 557-564.