



# Photocatalytic oxidation of gaseous ammonia over fluorinated TiO<sub>2</sub> with exposed (001) facets



Hongmin Wu, Jinzhu Ma, Yaobin Li, Changbin Zhang\*, Hong He

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

## ARTICLE INFO

### Article history:

Received 17 September 2013

Received in revised form 6 January 2014

Accepted 13 January 2014

Available online 23 January 2014

### Keywords:

Photocatalysis

NH<sub>3</sub>

Fluorination

TiO<sub>2</sub>

Indoor air quality

## ABSTRACT

A surface-fluorinated TiO<sub>2</sub> (F-TiO<sub>2</sub>) catalyst was synthesized by a hydrothermal method using hydrofluoric acid (HF) solution as a capping agent, and defluorinated TiO<sub>2</sub> (D-TiO<sub>2</sub>) was next obtained by washing the F-TiO<sub>2</sub> with NaOH solution. The as-prepared catalysts were tested for the photocatalytic oxidation (PCO) of gaseous NH<sub>3</sub> under UV light. The F-TiO<sub>2</sub> catalyst exhibited remarkable activity for NH<sub>3</sub> removal, about twice as high as that of the commercial catalyst P25. In contrast, D-TiO<sub>2</sub> showed an obvious decrease in PCO activity. The catalysts were characterized by X-ray diffractometry (XRD), Brunauer–Emmett–Teller (BET) adsorption analysis, High-resolution Transmission electron microscopy (HR-TEM), and X-ray photoelectron spectroscopy (XPS). The results showed that the surface fluorination process formed the surface ≡Ti–F group and also increased the percentage of reactive (001) facets to about 50%; the surface defluorination removed the fluorine (F) element from the F-TiO<sub>2</sub> surface but showed no influence on the percentage of reactive (001) facets. By comparing the specific activities of the catalysts, we found that both the active (001) facets and the surface ≡Ti–F group contributed to the improvement of the PCO activity, while the surface ≡Ti–F group plays the dominant role. The ≡Ti–F group could retard the recombination of photogenerated electrons and holes, which is possibly the major reason for the excellent activity of the F-TiO<sub>2</sub> catalyst.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

More and more attention has been paid to indoor air quality, since people spend almost 90% of their time inside buildings [1]. Gaseous ammonia (NH<sub>3</sub>), released from walls containing urea or ammonia compound-based antifreeze admixtures, is one of the major indoor air pollutants, particularly in China [2,3]. NH<sub>3</sub> is an alkaline gas with a pungent odor and is harmful to the environment and people's health. Long-time exposure to NH<sub>3</sub> can cause irritation of the skin, throat, lungs and eyes, affect the respiratory system and even cause permanent damage to the organs [3]. Therefore, it is of great interest to eliminate indoor air NH<sub>3</sub> to meet environmental regulations and health needs.

NH<sub>3</sub> can be eliminated by traditional remediation techniques, such as adsorption and ventilation, but they cannot eliminate NH<sub>3</sub> completely [4]. Selective catalytic oxidation (SCO) is an effective method to degrade NH<sub>3</sub>, but the oxidation reaction generally requires a high temperature [5–7]. Photocatalytic oxidation (PCO) could eliminate the indoor air pollutants such as formaldehyde and

volatile organic compounds under ultraviolet (UV) light irradiation at ambient temperature; therefore, it is a promising method for indoor air NH<sub>3</sub> destruction [8–11]. A few studies have been focused on the photocatalytic removal of gaseous NH<sub>3</sub>. Several types of modified TiO<sub>2</sub>-based photocatalysts such as TiO<sub>2</sub>-activated carbon composites [12,13], woven fabric-supported P25 [14,15] and latex paint-supported film nano-TiO<sub>2</sub> [16,17] have been evaluated for the PCO of NH<sub>3</sub> under UV light irradiation. The product distribution during the PCO of NH<sub>3</sub> has been investigated by FTIR or GC/GC–MS, and N<sub>2</sub> was found to be the main gaseous product; N<sub>2</sub>O, NO<sub>2</sub><sup>–</sup> and NO<sub>3</sub><sup>–</sup> were registered as the major by-products [12,18–20]. In general, the catalysts studied for the PCO of NH<sub>3</sub> reactions were anatase TiO<sub>2</sub> supported catalysts or the commercial catalyst P25. There are few studies focusing on the development of new types of catalysts for improving the photocatalytic activity of NH<sub>3</sub> removal.

Recently, anatase TiO<sub>2</sub> with exposed (001) facets has drawn great attention since Yang et al. prepared anatase TiO<sub>2</sub> microcrystals with 47% highly reactive (001) facets [21–30]. The average surface free energy of (001) facets is 0.90 J/m<sup>2</sup>, which is higher than those of (100) (0.53 J/m<sup>2</sup>) and (101) facets (0.44 J/m<sup>2</sup>) [31]. The majority of exposed facets of anatase TiO<sub>2</sub> are normally (101) due to it having the lowest surface energy under common conditions. In controllable synthesis of TiO<sub>2</sub> with exposed (001) facets, fluorine has been commonly used as a morphology-controlling

\* Corresponding author. Tel.: +86 10 62849121; fax: +86 10 62849121.  
E-mail address: [cbzhang@rcees.ac.cn](mailto:cbzhang@rcees.ac.cn) (C. Zhang).

agent to lower the surface energy in order to expose the reactive (001) facets [23,32,33]. Anatase TiO<sub>2</sub> with a high percentage of the reactive (001) facets has exhibited excellent photoreactivity, even much better than pure anatase TiO<sub>2</sub> or commercial P25 in photocatalytic reactions, such as the oxidation of acetone [23], OH radical generation [24] and the degradation of methylene orange (MO) [34] and methylene blue (MB) [35], etc. However, it is also reported that, compared with the other two facets, (001) facets are not always more reactive for some reactions, such as the reaction of hydrogen generation under UV light irradiation [36,37]. In addition, surface fluorination also showed some influence on the activity by retarding the recombination of the photogenerated electrons and holes, since the negative electrons and positive holes can selectively migrate to the specific exposed crystal face [23].

In this study, anatase TiO<sub>2</sub> with exposed (001) facets was synthesized via a hydrothermal route using HF as capping agent [23]. The catalysts were tested for the PCO of NH<sub>3</sub> reaction under UV light irradiation at room temperature. The effects of both the (001) facet percentage and the surface fluorination on the TiO<sub>2</sub> activity for the PCO of NH<sub>3</sub> reaction were examined in detail.

## 2. Experimental

### 2.1. Catalyst preparation

Pure anatase TiO<sub>2</sub> and fluorinated TiO<sub>2</sub> (F-TiO<sub>2</sub>) were prepared using a hydrothermal route similar to that reported by Yu et al. [23]. 3 mL of distilled water or hydrofluoric acid solution (with a concentration 40 wt%) (AR, China) were dropwise added into 25 mL of tetrabutyl titanate (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, CP, China) in a Teflon-lined autoclave at room temperature and under magnetic stirring. Then the Teflon-lined autoclave was kept at 190 °C for 24 h. After hydrothermal reaction, the precipitates were collected, washed with ethanol and distilled water four times, and then dried in an oven at 60 °C overnight.

The defluorinated TiO<sub>2</sub> (D-TiO<sub>2</sub>) was next obtained by washing the F-TiO<sub>2</sub> with NaOH solution. 1000 mg of the powder F-TiO<sub>2</sub> was reacted in 50 mL of 0.1 M NaOH solution under magnetic stirring for 10 h in the dark. Then the mixture was washed by dilute HCl solution and distilled water several times until no F<sup>-</sup> was detected in the filtrate. The collected precipitant was dried at 60 °C overnight.

### 2.2. Characterization of catalysts

Nitrogen adsorption–desorption isotherms were obtained at –196 °C using a Quantasorb-18 automatic instrument (Quanta Chrome Instrument Co). Specific surface areas were computed from these isotherms by applying the Brunauer–Emmett–Teller (BET) method. The pore size distribution was calculated from the desorption branch of the nitrogen isotherm by the BJH (Barrett–Joyner–Halenda) method. Powder X-ray diffraction (XRD) measurements of the catalysts were carried out on a PANalytical X'Pert Pro diffractometer using Cu K $\alpha$  radiation operating at 40 kV and 40 mA. The patterns were taken over the  $2\theta$  range from 10° to 90° with a step size of 0.026°. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEM-2011 electron microscope (JEOL, Japan). Field emission scanning electronic microscopy (FE-SEM) measurements were performed on a SU-8020 electron microscope (Hitachi, Japan). Diffuse-reflectance UV–vis spectra were obtained on a UV-1700 (SHIMADZU) spectrometer. The range was 190–800 nm and the scan rate was 120 nm/min. Photoluminescence (PL) spectra were measured on a Fluorescence Spectrophotometer (F-4500, Hitachi, Japan). The exciting wavelength was 300 nm, the scanning speed was 240 nm/min, the PMT

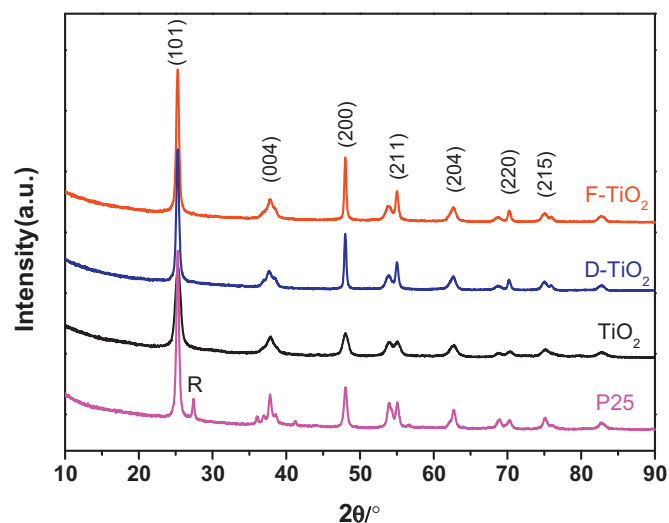


Fig. 1. XRD patterns of pure TiO<sub>2</sub>, F-TiO<sub>2</sub>, D-TiO<sub>2</sub> and P25 catalysts.

voltage was 400 V and the widths of the excitation and emission slits were 5.0 nm. X-ray photoelectron spectroscopy (XPS) of the catalysts was performed on a scanning X-ray microprobe (Axis Ultra, Kratos Analytical Ltd.) using Al K $\alpha$  radiation (1486.7 eV). All the binding energies were calibrated using the C 1s peak (BE = 284.8 eV) as standard.

### 2.3. Catalytic evaluation of catalysts

The catalyst evaluations for photocatalytic removal of gaseous NH<sub>3</sub> were performed in a black-colored box with a 500 W ultra-violet high pressure mercury lamp in a continuous flow system. The intensity of the UV light irradiation with peak wavelength at 365 nm on the catalysts' surface was 0.46 mW/cm<sup>2</sup>. There was a fan above the lamp and a circulated cooling system under the vessel to control the reaction temperature at 24 °C. 100 mg catalyst was dispersed in water and then the turbid solution was spread over a round stainless steel sample dish with diameter of 5.5 cm. The sample must be dry before being used. The reactant gas was 50 ppm NH<sub>3</sub>, 20 vol% O<sub>2</sub>, and balance N<sub>2</sub> with a total flow rate of 200 mL/min, and the relative humidity was 50%. The inlet and outlet gases were monitored by an FTIR (Nicolet 380) equipped with a 2 m gas cell.

## 3. Results and discussion

### 3.1. Phase structure and morphology

XRD patterns of TiO<sub>2</sub> catalysts were measured to characterize the bulk crystalline structures of the TiO<sub>2</sub> samples, and the results are shown in Fig. 1. Different from the commercial P25, the as-prepared catalysts only presented the anatase phase with peaks at  $2\theta = 25.3^\circ$  (101),  $37.8^\circ$  (004),  $48.1^\circ$  (200),  $54.0^\circ$  (105) and  $55.1^\circ$  (211) (JCPDS no. 21-1272), with good crystallinity. The crystal sizes of TiO<sub>2</sub> were calculated from the half-width of peaks using Scherrer's formula ( $d = 0.9\lambda / \beta \cos\theta$ ) and the results are shown in Table 1. It can be seen that the crystal size of F-TiO<sub>2</sub> is larger than that of pure TiO<sub>2</sub> as a result of the fluoride addition, which can facilitate the growth of crystallites [38]. The defluorination process had no influence on the crystal structures of samples; D-TiO<sub>2</sub> showed an XRD pattern and crystal size similar to that of F-TiO<sub>2</sub>.

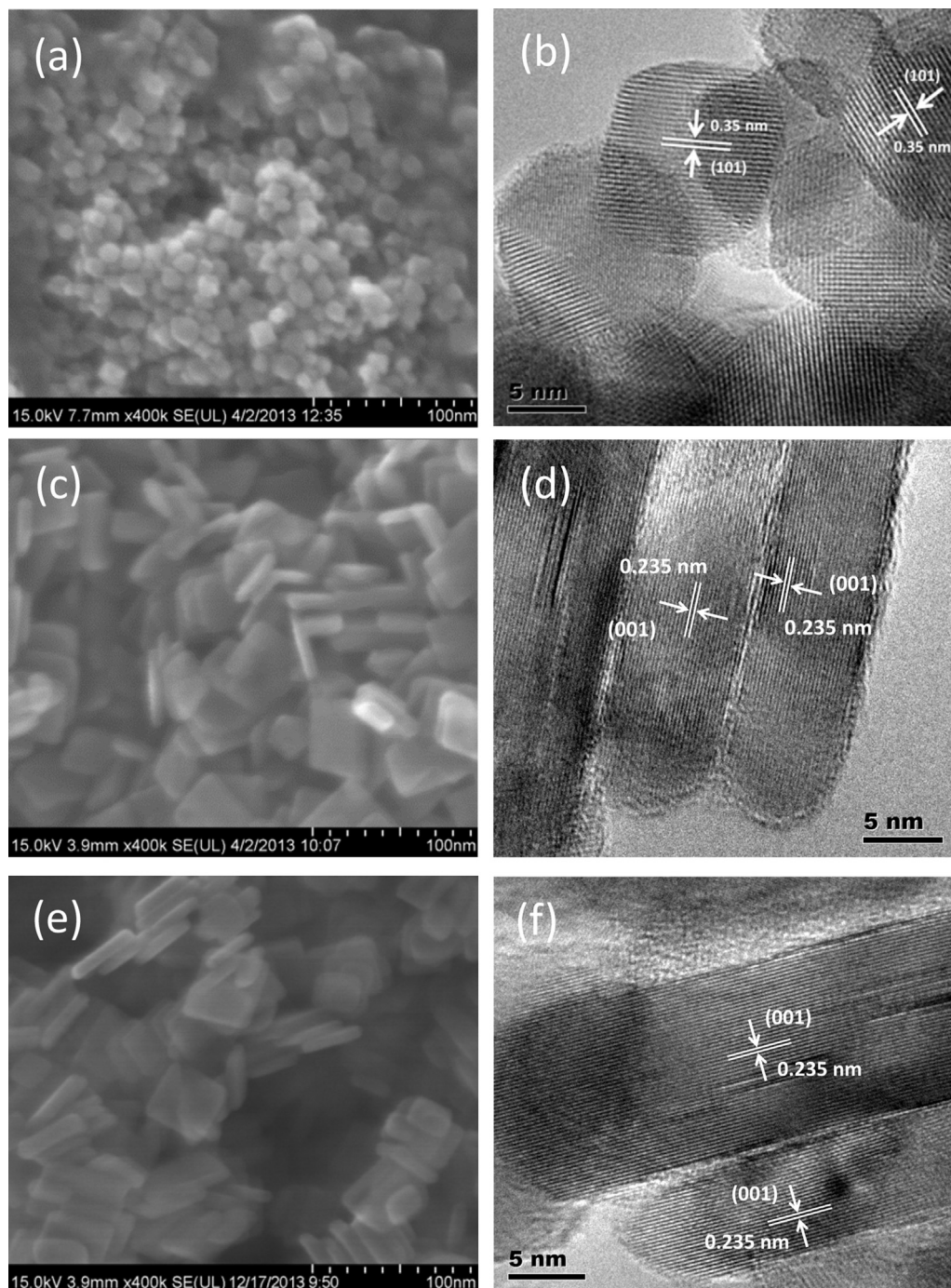
FE-SEM and HR-TEM images of the catalysts are shown in Fig. 2. From the FE-SEM image of the pure TiO<sub>2</sub> (Fig. 2a), we can see that the TiO<sub>2</sub> particle is regular in shape with average particle size of

**Table 1**  
Structural parameters of pure TiO<sub>2</sub>, F-TiO<sub>2</sub>, D-TiO<sub>2</sub> and P25.

Sample	SSA (m <sup>2</sup> /g)	Pore diameter (nm)	Pore volume (cm <sup>3</sup> /g)	Crystal size (nm)	Percentage of (001) (%)
TiO <sub>2</sub>	140.1	5.44	0.19	11.5	20.1
F-TiO <sub>2</sub>	86.2	14.8	0.32	19.4	49.3
D-TiO <sub>2</sub>	86.7	17.7	0.38	19.5	49.3
P25	59.1	11.8	0.17	20.8	17.7

about 11 nm, which is in accordance with the results of XRD. The HR-TEM image of pure TiO<sub>2</sub> (Fig. 2b) shows that the lattice spacing is 0.35 nm, corresponding to the (101) planes of anatase TiO<sub>2</sub>, indicating that the pure TiO<sub>2</sub> has mainly (101) facets exposed. The FE-SEM and HR-TEM images of F-TiO<sub>2</sub> (Fig. 2c and d) show

that the as-prepared F-TiO<sub>2</sub> consists of regular sheet-shaped structures, with an average side length of about 30 nm and an average thickness of about 10 nm. In addition, the HR-TEM image (Fig. 2d) directly shows that the lattice spacing parallel to the top and bottom facets is 0.235 nm, corresponding to the (001) planes, indicating



**Fig. 2.** FE-SEM image and HR-TEM image of pure TiO<sub>2</sub> (a and b), F-TiO<sub>2</sub> (c and d) and D-TiO<sub>2</sub> (e and f) catalysts.



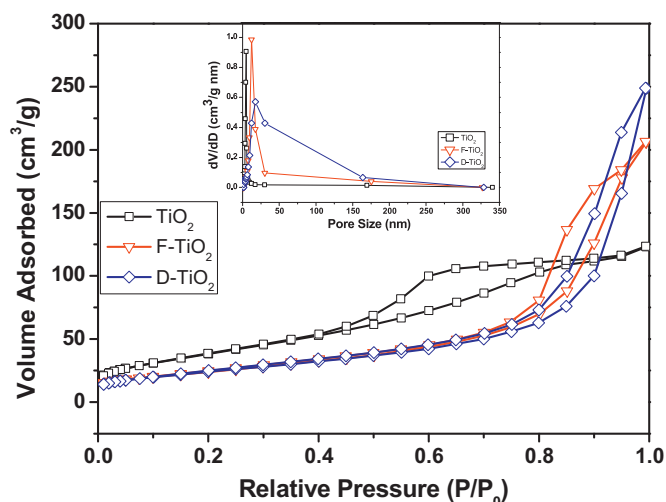


Fig. 3. Nitrogen adsorption–desorption isotherms of the  $\text{TiO}_2$  samples and their pore size distribution curves (inset).

that the exposed facets for F- $\text{TiO}_2$  are predominantly (001). The further defluorination process did not change the crystal structure and morphology of D- $\text{TiO}_2$ , and its active (001) facets remained intact (Fig. 2e and f). Based on the XRD results, SEM and HR-TEM images, we calculated the percentage of exposed (001) facets [35,37], and the data are shown in Table 1. It is indicated that the percentage of (001) facets for F- $\text{TiO}_2$  is 49.3%, which is much higher than that of pure  $\text{TiO}_2$  (20.1%). Moreover, the D- $\text{TiO}_2$  catalyst had a percentage of (001) facets equal to the F- $\text{TiO}_2$  catalyst, further proving that the defluorination process had no effect on the crystal structure of the samples.

### 3.2. BET surface area and pore size distribution

Nitrogen adsorption–desorption isotherms were measured to determine the textural structures of  $\text{TiO}_2$  samples and the results are shown in Table 1 and Fig. 3. The as-prepared anatase  $\text{TiO}_2$  presented a  $140.1 \text{ m}^2/\text{g}$  BET surface area,  $5.44 \text{ nm}$  pore diameter and  $0.19 \text{ cm}^3/\text{g}$  pore volume. The surface fluorination resulted in a sharp

drop in the BET surface area but a sharp increase in the pore size and pore volume of F- $\text{TiO}_2$  due to growth of  $\text{TiO}_2$  crystallites [23,39]. In contrast, the defluorination process did not induce much difference in BET surface area, pore diameter and pore volume of samples. As shown in Fig. 3, the isotherm of pure  $\text{TiO}_2$  was type IV and the hysteresis loop was of type H2, indicating that the pure  $\text{TiO}_2$  might mainly consists of the ink-bottle pores. The pore size distribution of the pure  $\text{TiO}_2$  presented a narrow range of 2.0–7.0 nm with a peak of about 5 nm. The fluorination resulted in the change of the hysteresis loop from type H2 to H3, showing that the pore structure is dramatically altered after the fluorination and the slit-like pores is formed due to the aggregation of  $\text{TiO}_2$  nanosheets. In addition, the pore size distribution of F- $\text{TiO}_2$  is wider than that of pure  $\text{TiO}_2$ , indicating the coexistence of both mesopores and macropores, which can facilitate the transport of reactant and product molecules in photocatalytic reactions [23]. The D- $\text{TiO}_2$  also showed the H3 type hysteresis loop but with a wider pore size distribution than that of F- $\text{TiO}_2$  possibly due to the fluorine removal in the pores.

### 3.3. XPS analysis

XPS spectra of pure  $\text{TiO}_2$ , F- $\text{TiO}_2$  and D- $\text{TiO}_2$  are shown in Fig. 4. These catalysts all contained C, Ti, and O elements, with sharp photoelectron peaks appearing at binding energy 285 eV (C 1s), 458 eV (Ti 2p) and 531 eV (O 1s). The C element is ascribed to residual carbon. The fluoride peak at binding energy 684.5 eV (F 1s) only appears in the F- $\text{TiO}_2$  sample, indicating the formation of surface fluoride ( $\equiv\text{Ti-F}$ ) by a ligand exchange reaction between  $\text{F}^-$  and the surface hydroxyl group on the  $\text{TiO}_2$  surface [40–44]. No peak for  $\text{F}^-$  ions in the lattice at 688.5 eV was observed in the spectra, because the hydrothermal process could prevent the substitution of  $\text{F}^-$  for  $\text{O}^{2-}$  in the lattice of  $\text{TiO}_2$  [21,39,40,45]. The fluoride peak in the D- $\text{TiO}_2$  almost disappeared after defluorination, indicating that the surface fluorine atoms were removed by NaOH washing for 10 h [46].

### 3.4. UV–vis and PL analysis

UV–vis diffuse reflectance spectra were measured to investigate the optical properties of the catalysts, and the results are shown in Fig. 5. The pure  $\text{TiO}_2$ , F- $\text{TiO}_2$  and D- $\text{TiO}_2$  showed similar adsorption

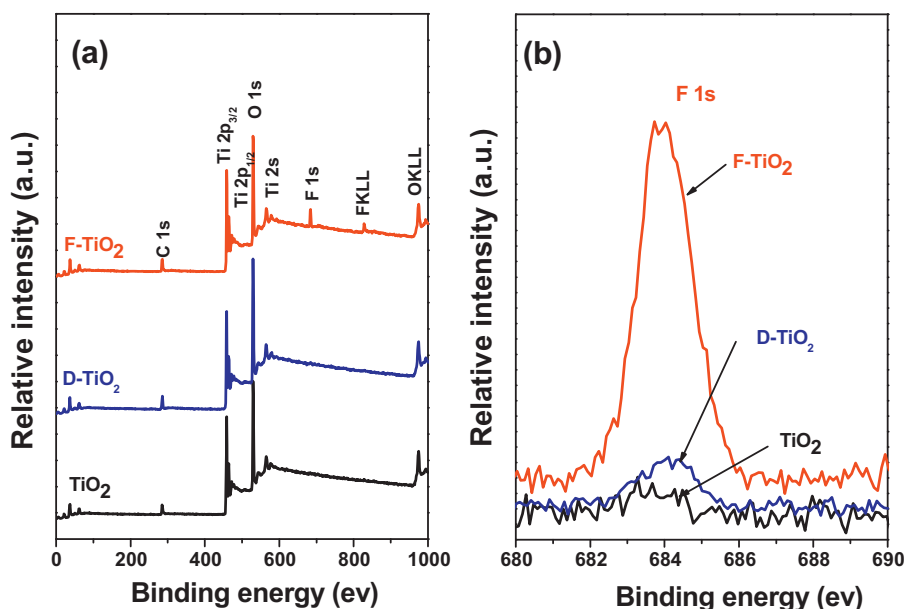


Fig. 4. XPS survey spectra (a) and high resolution XPS spectra of F 1s (b) of pure  $\text{TiO}_2$ , F- $\text{TiO}_2$  and D- $\text{TiO}_2$ .

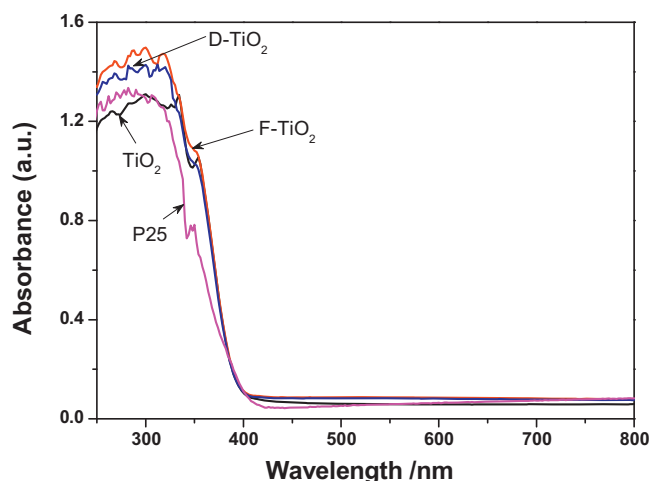


Fig. 5. UV-vis diffuse reflection spectra of pure  $\text{TiO}_2$ , F- $\text{TiO}_2$ , D- $\text{TiO}_2$  and P25.

edge regions with an obvious blue shift compared with P25, indicating that as-prepared catalysts have a wider band gap than P25. It has been reported that a wider band gap may cause a higher oxidation power for the photo-induced holes [27]. Moreover, the absorbance intensity of the F- $\text{TiO}_2$  catalyst in the UV region is strongest among the series of samples, which will favor improvement of the photocatalytic activity.

Photoluminescence (PL) spectra of catalysts were next measured to investigate the efficiency of charge carrier trapping, migration, and transfer and the separation of photogenerated electron-hole pairs [47]. It was reported that a weaker PL emission signal is commonly indicative of higher photocatalytic activity [48,49]. Fig. 6 shows the measured PL spectra, and all samples presented similar emission bands. The broad emission band at around 400 nm is attributed to the emission of the band gap transition, and the other five peaks ranging from 440 nm to 500 nm are due to surface oxygen vacancies, impurities and defects, respectively [50]. It is noteworthy that the F- $\text{TiO}_2$  sample has the lowest PL signals among the as-prepared catalysts and P25. It has been reported that the  $\equiv\text{Ti}-\text{F}$  group on the F- $\text{TiO}_2$  surface could act as an electron-trapping site to trap the photo-generated electrons, by holding trapped electrons and then transferring them to  $\text{O}_2$  adsorbed on the  $\text{TiO}_2$  surface [23,34,39]. Thus, the  $\equiv\text{Ti}-\text{F}$  group accounts for the very low PL spectra intensity of F- $\text{TiO}_2$ . In addition, the D- $\text{TiO}_2$  catalyst still showed a lower PL signal than pure  $\text{TiO}_2$  and P25, which

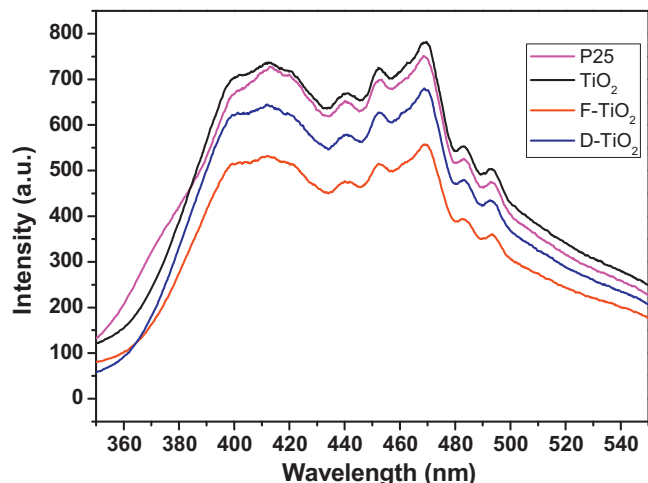


Fig. 6. PL spectra of pure  $\text{TiO}_2$ , F- $\text{TiO}_2$ , D- $\text{TiO}_2$  and P25.

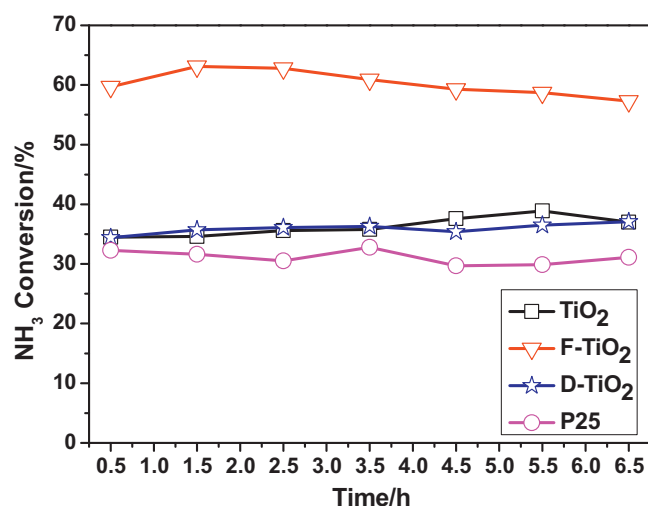


Fig. 7. Activities of  $\text{TiO}_2$ , F- $\text{TiO}_2$ , D- $\text{TiO}_2$  and P25 catalysts for the PCO of  $\text{NH}_3$  as a function of UV light irradiation time.

should be attributed to the presence of about 50% percentage of exposed (001) facets, because a percentage of (001) facets is also beneficial for the transfer and separation of photo-generated electrons and holes [23].

### 3.5. Photocatalytic activity test

The prepared catalysts were evaluated for the PCO of  $\text{NH}_3$  under UV light (365 nm) at room temperature. Fig. 7 presents the  $\text{NH}_3$  conversion with time on-stream over all catalysts and Fig. 8 shows the average  $\text{NH}_3$  conversion of the catalysts. All the catalysts showed stable activities during the tests. It is well known that P25 has excellent photocatalytic activity. Compared with P25, the as-prepared catalysts using the hydrothermal method presented better activity for the PCO of  $\text{NH}_3$ . The removal efficiency of the pure  $\text{TiO}_2$  catalyst was about 35%. The F- $\text{TiO}_2$  catalyst presented the best photocatalytic activity with above 60%  $\text{NH}_3$  removal efficiency, which is about twice as high as that of P25. The defluorination process resulted in a obvious decrease in photocatalytic activity, and the  $\text{NH}_3$  removal efficiency over the D- $\text{TiO}_2$  catalyst was only about 36%, similar to that of the pure  $\text{TiO}_2$  catalyst.

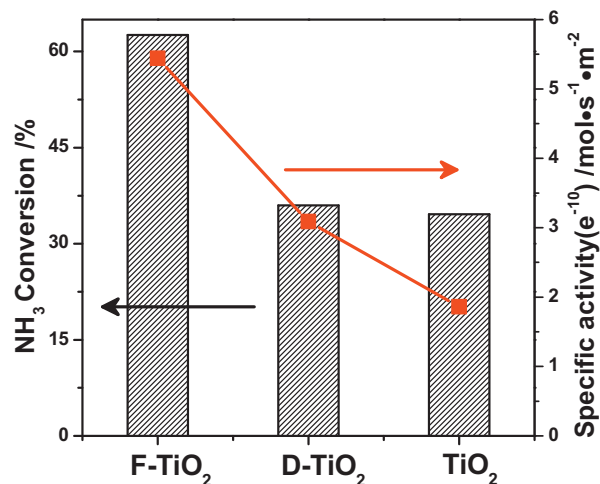


Fig. 8. Comparison of the average photocatalytic activities (column) and the specific activities (line + symbol) of  $\text{TiO}_2$ , F- $\text{TiO}_2$  and D- $\text{TiO}_2$  catalysts.

As shown in Table 1, the BET surface areas of as-prepared catalysts were very different from each other. Therefore, we calculated the specific activities normalized by surface area to exclude the effect of BET surface area on activity, and the results are given in Fig. 8. The F-TiO<sub>2</sub> exhibited the highest specific activity among the samples. The specific activity sharply dropped after defluorination, however, the D-TiO<sub>2</sub> still presented much higher specific activity than the pure TiO<sub>2</sub>. These findings show that the PCO of NH<sub>3</sub> reaction is closely related to both the percentage of exposed active (001) facets and the surface fluorination.

It has been reported that the (001) surface of anatase TiO<sub>2</sub> is more reactive than the stable (101) surface, and is normally the dominant active site for the PCO reactions [23,51]. In addition, the surface ≡Ti-F group can reduce the recombination rate of the photo-generated electrons and holes, thus leading to the better photocatalytic activity. Therefore, the surface fluorinated F-TiO<sub>2</sub> catalyst, with a high percentage of exposed active (001) facets, exhibited excellent activity for the PCO of NH<sub>3</sub>. The defluorination process removed the ≡Ti-F groups from the catalyst surface and partially lost the ability to decrease the recombination rate of electrons and holes; however, the 50% percentage of active (001) facets remained unchanged during the process. Therefore, although the specific activity of the D-TiO<sub>2</sub> obviously dropped after defluorination, it was still much higher than the pure TiO<sub>2</sub>. In addition, as shown in Fig. 8, the specific activities of F-TiO<sub>2</sub>, D-TiO<sub>2</sub> and pure TiO<sub>2</sub> were about  $5.44 \times 10^{-10}$ ,  $3.06 \times 10^{-10}$  and  $1.86 \times 10^{-10}$  mol/s/m<sup>2</sup>, respectively. It is clear that the surface ≡Ti-F group plays a more important role than the active (001) facets in promoting the activity of PCO of NH<sub>3</sub>.

#### 4. Conclusions

Fluorinated TiO<sub>2</sub> nanosheets (F-TiO<sub>2</sub>), defluorinated catalyst (D-TiO<sub>2</sub>) and pure TiO<sub>2</sub> nanoparticles were prepared by using a hydrothermal method and were evaluated for the PCO of gaseous NH<sub>3</sub>. The F-TiO<sub>2</sub> catalyst showed the best activity among the series of catalysts. It is shown that both the exposure of a high percentage of (001) facets and the presence of surface ≡Ti-F groups contributed to the excellent activity of F-TiO<sub>2</sub>, but the surface fluorination played a dominant role compared to that of the active(001) facets in enhancing the activity of the PCO of NH<sub>3</sub>.

#### Acknowledgments

This work was financially supported by the Program of the Ministry of Science and Technology of China (2010AA064905), the Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDB05050600) and the National Natural Science Foundation of China (21077117).

#### References

- [1] A. Jones, *Atmos. Environ.* 33 (1999) 4535–4564.
- [2] Z.Y. Meng, W.L. Lin, X.M. Jiang, P. Yan, Y. Wang, Y.M. Zhang, X.F. Jia, X.L. Yu, *Atmos. Chem. Phys.* 11 (2011) 6139–6151.
- [3] Z. Bai, Y. Dong, Z. Wang, T. Zhu, *Environ. Int.* 32 (2006) 303–311.
- [4] K. Kim, C. Shin, *Carbon Sci.* 2 (2001) 109–112.
- [5] A. Akah, C. Cundy, A. Garforth, *Appl. Catal., B* 59 (2005) 221–226.
- [6] X.Z. Cui, J. Zhou, Z.Q. Ye, H.R. Chen, L. Li, M.L. Ruan, J.L. Shi, *J. Catal.* 270 (2010) 310–317.
- [7] L. Zhang, H. He, *J. Catal.* 268 (2009) 18–25.
- [8] F.N. Chen, X.D. Yang, Q. Wu, *Environ. Sci. Technol.* 43 (2009) 4606–4611.
- [9] J. Mo, Y. Zhang, Q. Xu, J.J. Lamson, R. Zhao, *Atmos. Environ.* 43 (2009) 2229–2246.
- [10] T. Guo, Z. Bai, C. Wu, T. Zhu, *Appl. Catal., B* 79 (2008) 171–178.
- [11] C. Chen, W. Ma, J. Zhao, *Chem. Soc. Rev.* 39 (2010) 4206–4219.
- [12] H. Hou, H. Miyafuji, H. Kawamoto, S. Saka, *J. Wood Sci.* 52 (2006) 533–538.
- [13] M. Nazir, J. Takasaki, H. Kumazawa, *Chem. Eng. Commun.* 190 (2003) 322–333.
- [14] Y.C. Dong, Z.P. Bai, R.H. Liu, T. Zhu, *Atmos. Environ.* 41 (2007) 3182–3192.
- [15] Y.C. Dong, Z.P. Bai, R.H. Liu, T. Zhu, *Catal. Today* 126 (2007) 320–327.
- [16] Q.J. Geng, Q.J. Guo, C.Q. Cao, Y.C. Zhang, L.T. Wang, *Ind. Eng. Chem. Res.* 47 (2008) 4363–4368.
- [17] Q.J. Geng, X.K. Wang, S.F. Tang, *Biomed. Environ. Sci.* 21 (2008) 118–123.
- [18] P.A. Kolinko, D.V. Kozlov, *Appl. Catal., B* 90 (2009) 126–131.
- [19] S. Yamazoe, T. Okumura, Y. Hitomi, T. Shishido, T. Tanaka, *J. Phys. Chem. C* 111 (2007) 11077–11085.
- [20] S. Yamazoe, T. Okumura, T. Tanaka, *Catal. Today* 120 (2007) 220–225.
- [21] H.G. Yang, C.H. Sun, S.Z. Qiao, J. Zou, G. Liu, S.C. Smith, H.M. Cheng, G.Q. Lu, *Nature* 453 (2008) 638–641.
- [22] X.Q. Gong, A. Selloni, *J. Phys. Chem. B* 109 (2005) 19560–19562.
- [23] Q. Xiang, K. Lv, J. Yu, *Appl. Catal., B* 96 (2010) 557–564.
- [24] H.G. Yang, G. Liu, S.Z. Qiao, C.H. Sun, Y.G. Jin, S.C. Smith, J. Zou, H.M. Cheng, G.Q. Lu, *J. Am. Chem. Soc.* 131 (2009) 4078–4083.
- [25] D.Q. Zhang, G.S. Li, X.F. Yang, J.C. Yu, *Chem. Commun.* (2009) 4381–4383.
- [26] J. Zhang, J. Wang, Z. Zhao, T. Yu, J. Feng, Y. Yuan, Z. Tang, Y. Liu, Z. Li, Z. Zou, *Phys. Chem. Chem. Phys.* 14 (2012) 4763–4769.
- [27] Y. Zhao, Q. Zhao, X. Li, Y. Hou, X. Zou, J. Wang, T. Jiang, T. Xie, *Mater. Lett.* 66 (2012) 308–310.
- [28] Y. Zheng, K. Lv, Z. Wang, K. Deng, M. Li, *J. Mol. Catal. A: Chem.* 356 (2012) 137–143.
- [29] Z. Zheng, B. Huang, X. Qin, X. Zhang, Y. Dai, M. Jiang, P. Wang, M.H. Whangbo, *Chem. Eur. J.* 15 (2009) 12576–12579.
- [30] S. Liu, J. Yu, M. Jaroniec, *Chem. Mater.* 23 (2011) 4085–4093.
- [31] M. Lazzeri, A. Vittadini, A. Selloni, *Phys. Rev. B: Condens. Matter* 63 (2001) 155409.
- [32] K. Lv, B. Cheng, J. Yu, G. Liu, *Phys. Chem. Chem. Phys.* 14 (2012) 5349–5362.
- [33] K. Lv, Q. Xiang, J. Yu, *Appl. Catal., B* 104 (2011) 275–281.
- [34] X.G. Han, Q. Kuang, M.S. Jin, Z.X. Xie, L.S. Zheng, *J. Am. Chem. Soc.* 131 (2009) 3152–3153.
- [35] F. Tian, Y. Zhang, J. Zhang, C. Pan, *J. Phys. Chem. C* 116 (2012) 7515–7519.
- [36] J. Pan, G. Liu, G.M. Lu, H.M. Cheng, *Angew. Chem. Int. Ed.* 50 (2011) 2133–2137.
- [37] T.R. Gordon, M. Cargnello, T. Paik, F. Mangolini, R.T. Weber, P. Fornasiero, C.B. Murray, *J. Am. Chem. Soc.* 134 (2012) 6751–6761.
- [38] J. Yu, S. Liu, H. Yu, *J. Catal.* 249 (2007) 59–66.
- [39] J. Yu, W. Wang, B. Cheng, B.-L. Su, *J. Phys. Chem. C* 113 (2009) 6743–6750.
- [40] H. Park, W. Choi, *J. Phys. Chem. B* 108 (2004) 4086–4093.
- [41] M. Herrmann, U. Kaluza, H. Boehm, *Z. Anorg. Allg. Chem.* 372 (1970) 308–313.
- [42] M.S. Vohra, S. Kim, W. Choi, *J. Photochem. Photobiol., A* 160 (2003) 55–60.
- [43] C. Minero, G. Mariella, V. Maurino, E. Pelizzetti, *Langmuir* 16 (2000) 2632–2641.
- [44] C. Minero, G. Mariella, V. Maurino, D. Vione, E. Pelizzetti, *Langmuir* 16 (2000) 8964–8972.
- [45] J.C. Yu, J. Yu, W. Ho, Z. Jiang, L. Zhang, *Chem. Mater.* 14 (2002) 3808–3816.
- [46] Q. Wang, C. Chen, D. Zhao, W. Ma, J. Zhao, *Langmuir* 24 (2008) 7338–7345.
- [47] J. Shi, J. Chen, Z. Feng, T. Chen, Y. Lian, X. Wang, C. Li, *J. Phys. Chem. C* 111 (2007) 693–699.
- [48] X.F. Chen, X.C. Wang, Y.D. Hou, J.H. Huang, L. Wu, X.Z. Fu, *J. Catal.* 255 (2008) 59–67.
- [49] Z.L. He, Z.F. Zhu, J.Q. Li, J.Q. Zhou, N. Wei, *J. Hazard. Mater.* 190 (2011) 133–139.
- [50] J.G. Yu, T.T. Ma, S.W. Liu, *Phys. Chem. Chem. Phys.* 13 (2011) 3491–3501.
- [51] A. Selloni, *Nat. Mater.* 7 (2008) 613–615.