



Facet-dependent performance of anatase TiO₂ for photocatalytic oxidation of gaseous ammonia



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ABSTRACT

Photocatalytic oxidation of gaseous ammonia (NH₃) at room temperature is an efficient method for the elimination of NH₃ emitted from indoor and outdoor sources, such as decorative materials, intensive live-stock farming, chemical processes, etc. Herein, we prepared the anatase TiO₂ with clean dominant {001}, {101} and {010} facets, and tested their photocatalytic activity for NH₃ oxidation. The test results show that the photocatalytic activity order for NH₃ oxidation is revealed as {001} > {101} > {010}. The catalysts were characterized by XRD, FE-SEM, XPS, UV-vis, in situ DRIFTS and TPD methods. It is indicated that TiO₂ with dominant {001} facets has the highest separation efficiency of the photogenerated charges among three catalysts. Since the photogenerated holes is responsible for initiating the first step of NH₃ oxidation, the TiO₂ with dominant {001} facets demonstrated the exceptional activity. In addition, the photocatalytic oxidation of NH₃ possibly follow the photo-iSCR mechanism. The photogenerated electrons activate O₂ and then participate in the formation of reactive intermediate NO_x followed by the photo-NH₃-iSCR to final products. The present study will improve our understanding about the performance of anatase TiO₂ for photocatalytic oxidation of NH₃.

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1. Introduction

Gaseous ammonia (NH₃) as one of the major air pollutants mainly stems from agriculture emissions and the release of decorative materials containing urea or ammonia compound-based antifreeze admixtures [1–4]. Excessive emissions of ammonia would give rise to a series of negative influences on environment and human health. Therefore, in order to meet the environmental regulations and health needs, it is necessary to develop the techniques for NH₃ removal. Traditional techniques, such as selective catalytic oxidation (SCO), can effectively remove NH₃. A number of catalysts such as Cu and Fe exchanged ZSM-5 [5,6], Ag/Al₂O₃ showed excellent SCO performance [7,8]. However, SCO of NH₃ often performed at high temperature (>433 K).

Since the discovery of photocatalytic splitting of water on TiO₂ in 1972, TiO₂ has been undoubtedly proven to be one of the best photocatalysts for pollutant removal due to its physical and chemical stability, low cost, easy availability, and unique electronic and optical properties [9–12]. Recently, the potential of photocatalytic elimination of NH₃ at room temperature has already been well recognized [13–16]. Yamazoe et al. compared the activity of photocatalytic oxidation of NH₃ (PCO) over various commercial TiO₂ [14]. In our previous study, we found that fluorine modified TiO₂ showed the excellent activity for PCO of NH₃ [17].

Since the synthesis of anatase TiO₂ with high percentage of {001} facets exposed was firstly reported by Lu et al. [18], facet-dependent photocatalytic properties of anatase TiO₂ nanocrystals with well-defined facets have received enormous research attention [19–26]. Generally, {101}, {001} and {010} facets are the three fundamental low-index facets of anatase TiO₂ crystals. The results of theoretically calculated surface energy showed that the surface energy of anatase TiO₂ increases in the order of {101} facet (0.44 J·m⁻²) < {010} facet (0.53 J·m⁻²) < {001} facet (0.90 J·m⁻²) [18]. Han et al. [27] found that {001} facets showed superior photodegradative activity for organic pollutants, while Pan et al. [19]

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pointed out that {010} or {101} facet of TiO₂ exhibited higher photoreactivity than {001} facets for the H₂ evolution reaction. Besides, {010} facet exposed anatase TiO₂ was demonstrated to be superior to {101} and {001} facets for the CO₂ reduction by Ye et al. [28]. Apparently, the activity order for the different facets of anatase TiO₂ is closely related to the photocatalytic reaction type.

There are three main factors influencing the activity of anatase TiO₂ with well-defined facets. (i) The different exposed facets have distinct band structure, which determine the separation efficiency of the photogenerated carriers in a photocatalytic reaction. Generally, the wider the band gap a semiconductor associate with the higher quantum efficiency [10]. (ii) The difference of preferential transport directions of photogenerated carriers with regard to the facet-dependent photocatalytic activity is believed to be an important factor. It was documented that {001} facets favor to trap holes as oxidative sites, while {101} facets incline to trap electrons as reductive sites [29,30]. (iii) A specific photocatalytic reaction has its own features, for example, CO₂ reduction should need more strongly reductive electrons [28], however, for many organic pollutants degradation, photogenerated holes direct oxidation or •OH indirect oxidation play a dominant role [31,32]. The activity order of a specific photocatalytic reaction over different exposed facet of anatase TiO₂ is determined by the combined effect of above factors.

In the present study, dominant {001}, {101}, {010} facet exposed anatase TiO₂ were controllably synthesized and were applied to the PCO of NH₃ under room temperature. Based on the results of XRD, SEM, XPS, UV-vis, DRIFTS and TPD characterization, the relationship between facet-dependent physico-chemical properties of TiO₂ and the performance of NH₃ oxidation was explored.

2. Experimental

2.1. Preparation of catalysts

T001: TiO₂ with exposed {001} facets (denoted as T001) was controllably prepared according to a modified HF hydrothermal method similar to that reported by Han et al. [27]. In a typical synthesis, 4 mL of hydrofluoric acid solution (40 wt.%) was added dropwise into the prepared Ti(OC₄H₉)₄ (25 mL) in a 100 mL Teflon-lined autoclave at room temperature under magnetic stirring, then the autoclave was sealed and heated at 190 °C for 24 h. After hydrothermal reaction, the white precipitate was collected and washed with ethanol and distilled water several times, then dried overnight in an oven at 60 °C and finally 550 °C calcination for 2 h.

T101: {101} facet exposed TiO₂ (denoted as T101) were synthesized by a two-step hydrothermal procedure similar to previous reports [24]. In the first step, 1 g of P25 was reacted hydrothermally with 70 mL KOH solution (10 M) in a Teflon-lined autoclave with a capacity of 100 mL at 200 °C for 48 h. The resulting precipitate was washed and neutralized using deionized water and dried at 60 °C. In the second step, the prepared potassium titanate (70 mg) was stirred in distilled water (70 mL) and heated in a 100 mL Teflon-lined autoclave at 170 °C for 24 h. The white precipitate was washed and dried at 100 °C.

T010: the route was similar to that of the T101 sample except that the second hydrothermal temperature was 200 °C.

2.2. Characterization

The crystalline structure of the photocatalysts was examined by powder X-ray diffractometer (XRD; X'Pert PRO, PANalytical, Netherlands) with Cu K α ($\lambda = 0.154\ 06\ \text{nm}$) radiation at 40 kV and 40 mA. The patterns were collected over the 2θ range from 10° to 90° with a scan step of 0.02°. The morphology of the photocatalysts were investigated using a SU8000 field emission scanning elec-

tron microscope (FE-SEM). The powder of a sample was deposited on a silicon wafer before FE-SEM measurements. The specific surface area was obtained at 77 K over the whole range of relative pressures, using a Quantachrome Quadrasorb SI-MP analyzer. The catalysts were degassed at 300 °C for 3 h prior to the N₂ physisorption. The BET equation was applied to calculate the Specific surface areas in the 0.05–0.3 partial pressure range from the adsorption isotherm. X-ray photoelectron spectroscopy (XPS) was measured on a Scanning X-ray Microprobe (AXIS Ultra, Kratos Analytical, Inc.), and the spectra were calibrated to the C 1s peak at 284.6 eV. The UV-vis diffuse reflection spectra (DRS) were obtained in air with Al₂O₃ as a reference with a diffuse reflectance UV-vis Spectrophotometer (U-3310, Hitachi).

The photochemical properties of the photocatalysts was investigated by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). A Fourier transform infrared spectrometer (Nicolet 380) equipped with a MCT detector was used to collect the infrared spectra, a spectra range from 4000 to 800 cm⁻¹ with a resolution of 4 cm⁻¹. The reaction cell has three windows, where two are ZnSe windows used for entry and exit of the detection infrared beam. The third quartz window is for the transmission of UV light during in situ photoreactions.

2.3. PCO activity tests

The photocatalytic activity tests for the oxidation of NH₃ were performed in a home-made flow reactor at ambient temperature. The stainless steel reactor was covered with a quartz plate. A round dish containing the photocatalyst was placed in the center of the reactor. 70 mg photocatalyst was dispensed on the round dish for each evaluation experiment. The light source is a 500 W commercial Hg lamp (Beijing TrusTech Science and Technology Co., China) with an optical filter ($\lambda = 365\text{--}366\ \text{nm}$), and the average light intensity was 10.5 mW/cm². The commercial Hg lamp was vertically placed outside the reactor, and the temperature of the photocatalyst was kept at 25 °C by water circulation. The concentrations of effluent gas, including NH₃, NO, NO₂ and N₂O, were measured by an FTIR spectrometer (Nicolet 380) equipped with 2 m gas cell and a DTGS detector. The reactant gas circularly flowed over the catalyst, and the volume of reactant gas was about 1.5 L and the initial concentration of reactant gas was 500 ppm NH₃, 20 vol% O₂, and N₂ balance.

3. Results and discussion

3.1. Structure characterization

The crystallographic structure of the as-synthesized samples was confirmed by the X-ray diffraction patterns (XRD). As shown in Fig. 1, the samples all show the peaks located at 25.28°, 36.95°, 37.8°, 38.58°, 48.05°, 53.89°, 55.96°, 62.69°, 68.76°, 70.31°, and 75.03°, which are indexed to {101}, {103}, {004}, {112}, {200}, {105}, {211}, {204}, {116}, {220}, and {215} facet of tetragonal anatase TiO₂ (JCPDS No. 21-1272), demonstrating that the synthesized T001, T101, and T010 are pure anatase TiO₂. Moreover, no typical peaks of other TiO₂ polymorph such as brookite or rutile were observed. Specific surface area (SSA) of T001, T101, and T010 are 84 m²/g, 41 m²/g and 27 m²/g, respectively.

The morphology of as-prepared catalysts was characterized by FE-SEM and the images are shown in Fig. 2. The T001 displays the typical nanosheet morphology with a length from 40 to 60 nm and a thickness of about 8 nm. The obtained T101 is mainly composed of octahedral bipyramids, and the average side length of the bipyramids is about 80 nm. T010 shows nanorods morphology with size of about 300 nm \times 50 nm. According to the reported method [24],

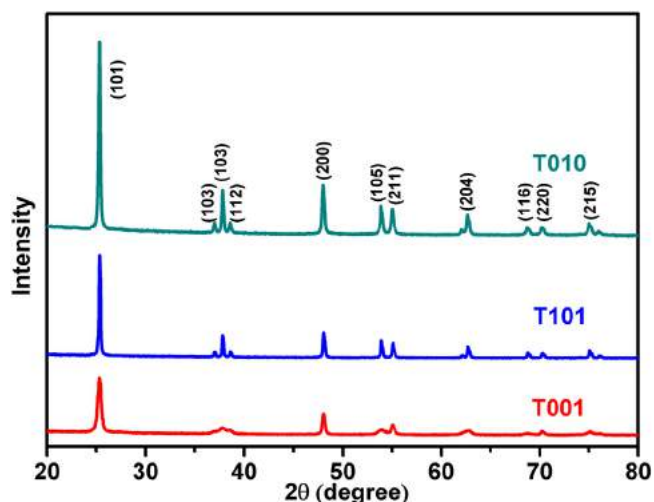


Fig. 1. XRD patterns of the T001, T101, and T010.

Table 1
Physiochemical Properties of T001, T101, and T010.

| Sample | Morphology | SSA (m ² /g) | Crystal size (nm) | Predominant facet (%) |
|--------|---------------|-------------------------|-------------------|-----------------------|
| T001 | nanosheets | 84 | 15.9 | 68.7 |
| T101 | nanooctahedra | 41 | 48.8 | 90.2 |
| T010 | nanorod | 27 | 60.4 | 83.3 |

the areas of each facet and total surface area were calculated based on FE-SEM images, and then the percentage of each predominant facet was obtained through dividing the total surface area by the area of {001}, {101} and {010} facets. As shown in Table 1, the percentages of {001}, {101}, and {010} are 68.7%, 90.2% and 83.3%, respectively.

The X-ray photoelectron spectra (XPS) were measured to analyze the surface chemical composition of the samples. Fig. 3a shows the XPS survey spectra of the T001, T101, and T010. The three samples all contain Ti, O, and C elements with sharp photoelectron peaks at binding energies of 458 eV (Ti2p), 531 eV (O1s), and 285 eV (C1s). The residual carbon from samples and hydrocarbon from the XPS instrument itself attributed to the carbon peak. Considering that hydrofluoric acid was used as a shape controlling agent in the synthesis of T001, in order to exclude the effects of surface fluorine [17], high temperature calcination was carried out to remove surface fluorine. XPS spectrum (Fig. 3b) showed that no F1s peak at 684 eV attributed to the formation of ≡Ti–F exist, confirming the absence of surface fluorine [17,33]. Therefore, we successfully synthesized the clean predominant TiO₂ with {001}, {101}, and {010} facets exposed.

3.2. PCO of NH₃ performance

T001, T101, and T010 were next tested for the PCO of NH₃. The reaction of NH₃ oxidation was negligible when control experiments were performed under UV irradiation in the absence of photocatalyst. Before UV irradiation, the catalyst–NH₃ flows were kept in dark for 2 h to reach the NH₃ adsorption–desorption equilibrium on the surface of catalyst. Fig. 4a plotted the C/C₀ with irradiation time, where “C₀” and “C” are the NH₃ concentration before and after UV irradiation, respectively. We found that an excellent linear relationship between log(C/C₀) and irradiation time (Fig. 4b), indicating that the PCO of NH₃ follows a pseudo-first-order kinetic. The results show that the photocatalytic activity order is T001 > T101 > T010. Specifically, T001 exhibited the highest PCO of NH₃ activity among three samples and its k reached 0.034 min^{−1}, which is 8.5 and 34

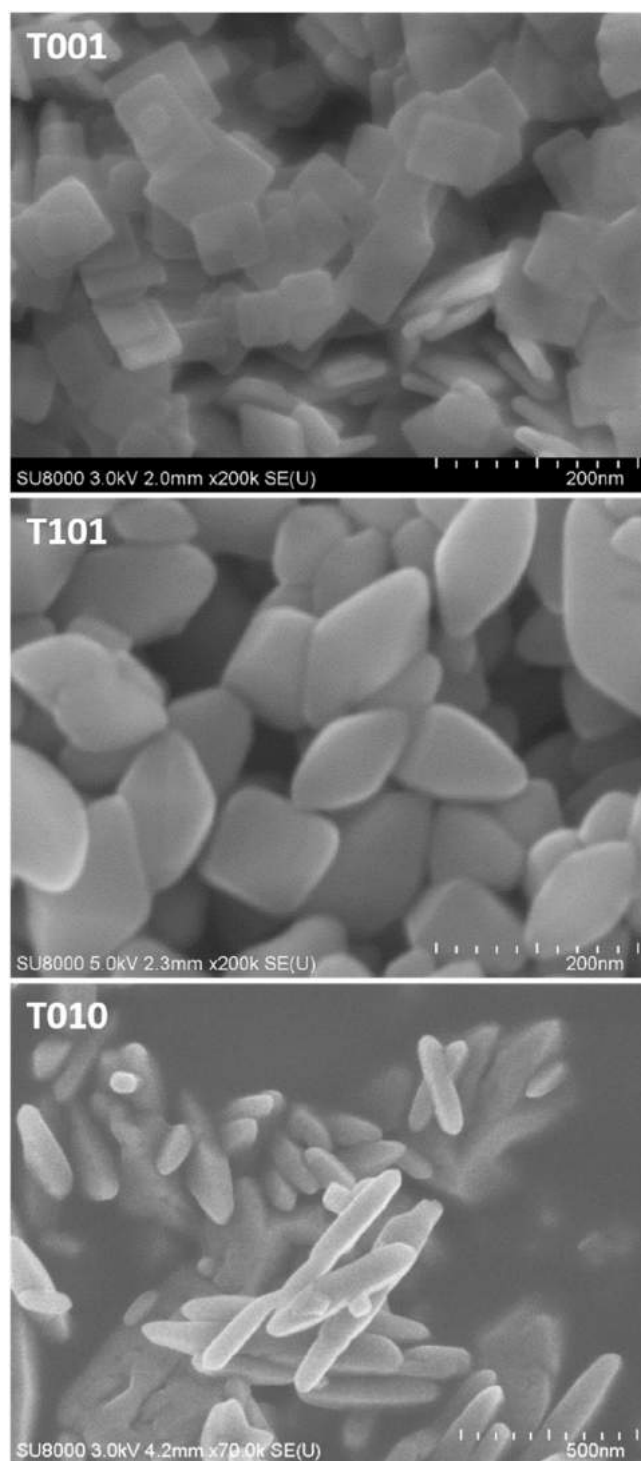


Fig. 2. SEM images of the T001, T101, and T010.

times higher than that of T101 and T010, respectively. Considering the effect of surface area, the rate constants were next normalized with the surface area, and the specific rate constant of T001 is 4.1 and 8.4 times as high as that of T101 and T010.

In addition, reliability and stability of a catalyst are very important for applications of photocatalysts. To evaluate this, repeated activity tests of T001 were carried out at regular intervals and the results are shown in Fig. 5. A relative stable NH₃ conversion was observed for four cycles without an apparent decrease, demonstrating the high stability of T001 photocatalyst.

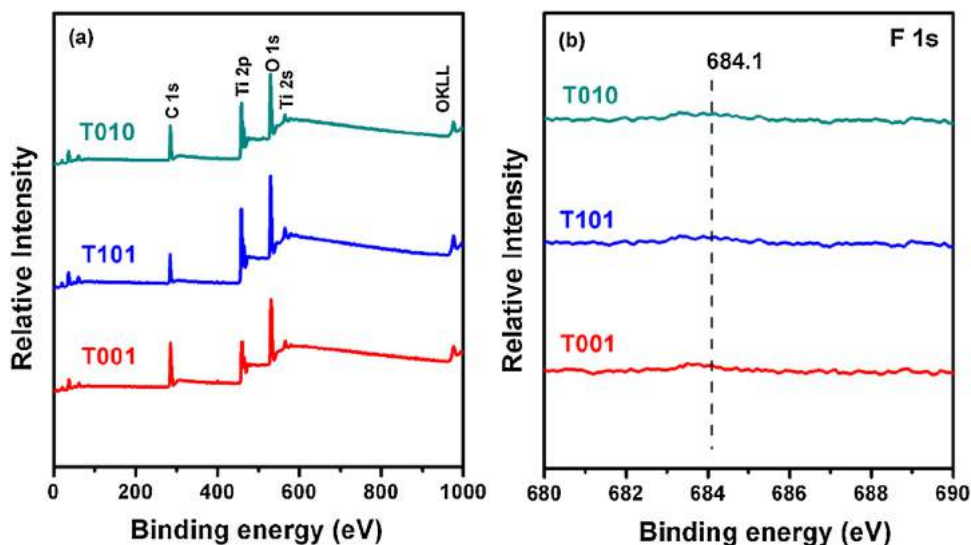


Fig. 3. XPS survey spectra (a) and high resolution XPS spectra of F 1s (b) of T001, T101, and T010.

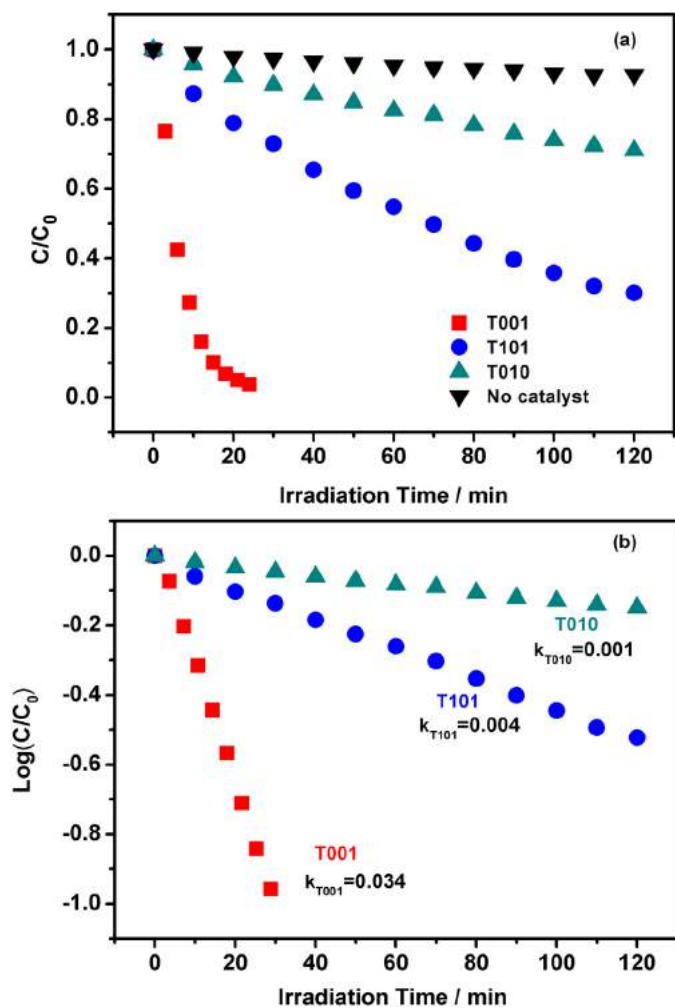


Fig. 4. Photocatalytic oxidation of NH_3 C/C_0 vs reaction time (a) and rate constants compare under UV irradiation over T001, T101, and T010 (b).

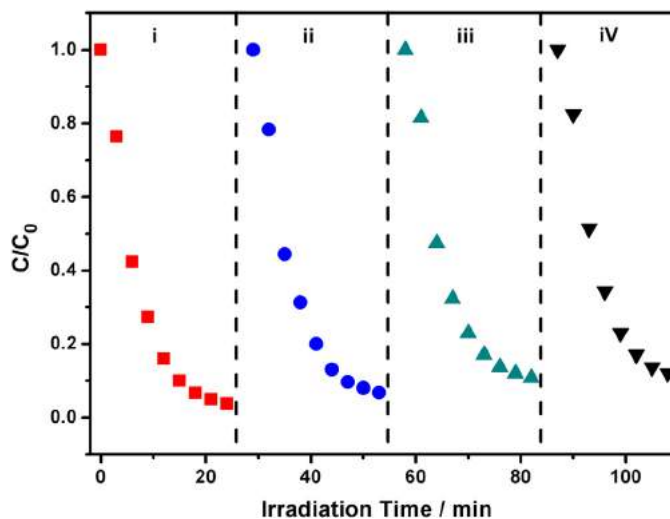


Fig. 5. Reusability of the T001 in four successive experimental runs for photocatalytic oxidation of NH_3 .

3.3. Reason analyses of the activity order for PCO of NH_3

3.3.1. Photochemical properties

The electronic structure is an important factor for the photocatalytic activity of anatase TiO_2 . Valence band (VB) and conduction band (CB) energy levels determine the redox potentials and the separation efficiency of the photogenerated carriers in a photocatalytic reaction [19,34]. Therefore, we investigated the electronic structures of the T001, T101, and T010. UV-vis absorption spectra (Fig. 6a) show that the absorption edge of T001 has an obvious redshift compared with T101 and T010, and the bandgaps of T001, T101, and T010 were calculated to be a value of approximately 3.23, 3.27, and 3.29 eV, respectively. Fig. 6b shows the X-ray photoelectron valence band spectra of the samples. The VB maxima of all three anatase TiO_2 crystals are at about 1.9 eV below the Fermi energy, which is consistent with the previous reports [34,35]. Then it can be induced that the CB minimum of T101 and T010 rise in contrast to T001, and the band structures of T001, T101, and T010 are illustrated in Fig. 6c. Pan et al. [19] pointed out that {101} and {010} facet exposed anatase TiO_2 should have superior photoreactivity to {001} facet, because more strongly reductive electrons can

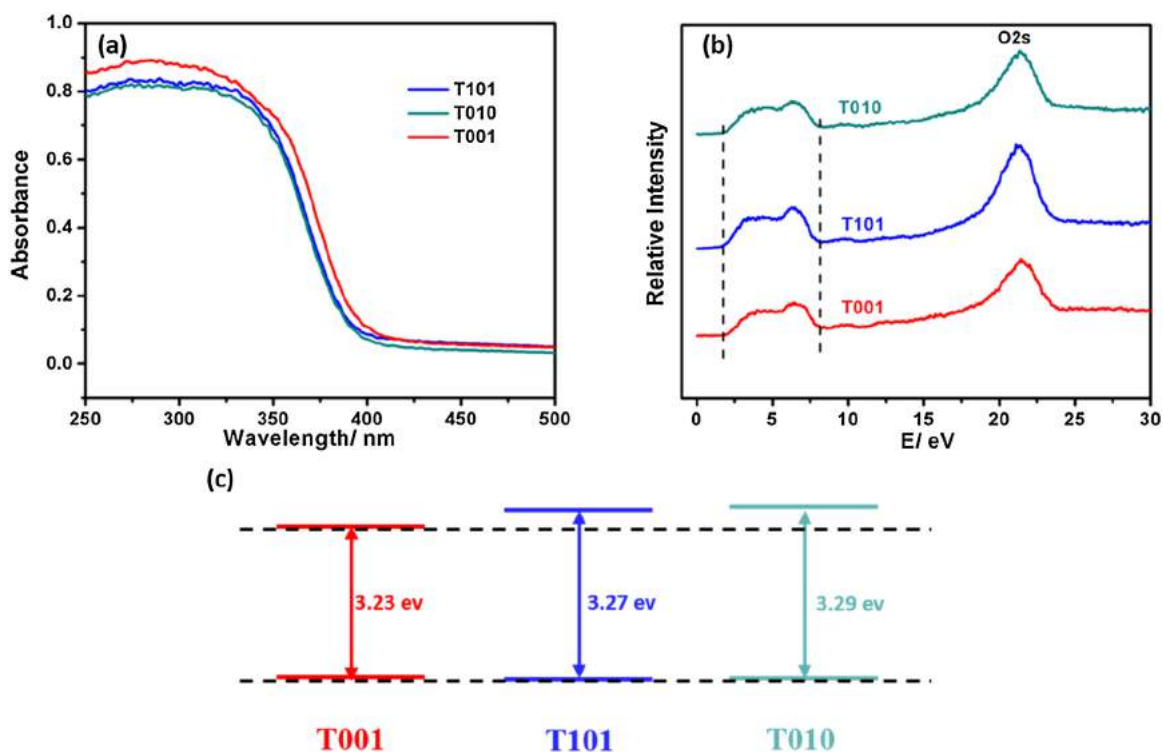


Fig. 6. UV/Vis absorption spectra of T001, T101, and T010 (a). VB XPS spectra of T001, T101, and T010. (b) VB and CB edges of T001, T101, and T010 (c).

be generated on {101} and {010} facets with a higher CB minimum. Active oxidizing species such as $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ can be produced via the reduction of O_2 by the CB electrons, then the organic pollutants can be well oxidized to CO_2 , H_2O and other products. However, we found that T101 and T010 exhibited worse performance to that of T001 in our activity tests (Fig. 5), it is therefore possible that photogenerated electrons is not very effective for the PCO of NH_3 . Ye et al. [28] also found that {101} and {010} facets exposed TiO_2 exhibited poor activity in dye degradation compared with {001} facets exposed TiO_2 , which may be accounted for in a similar way.

Photogenerated holes on VB band transfer to surface adsorbed H_2O or OH^- , initiating photooxidation reactions, is another extremely important step in the photocatalytic process and possibly plays a key role in the PCO of NH_3 [36–41]. Therefore, we next investigated the migration of photogenerated holes by in situ DRIFTS method using H_2O oxidation as a probe reaction. Infrared spectroscopy is very sensitive to the decrease or increase of surface H_2O and the accumulation of electrons on the TiO_2 surface resulting from H_2O oxidation by holes can usually absorb mid-IR (MIR) light and thus is able to be monitored by IR spectroscopy [42–45]. As shown in Fig. 7, in the absence of redox species except for H_2O , the UV irradiation caused no change in the IR spectra of T101 and T010, indicating that H_2O oxidation has not occurred and further demonstrating the rapid electron-hole pairs recombination on T101 and T010. However, in the case of the T001, the UV irradiation triggered an obvious increase in the background IR absorbance band ranging from 3000 to 1000 cm^{-1} , which is attributed to electron accumulation in the conduction band. Besides, a broad negative absorption band ranging from 3700 to 3000 cm^{-1} and narrow negative peak at 1628 cm^{-1} appeared, which were assigned to $\nu(\text{OH})$ and $\delta(\text{H}_2\text{O})$, respectively. These results revealed that the surface adsorbed H_2O on T001 is effectively oxidized by photogenerated holes under UV irradiation, demonstrating that the electron-hole pairs are well separated over T001 and more photogenerated holes were driven to the surface to oxidize the H_2O , which should be the main reason why T001 is much more active than T101 and T010 for the PCO of

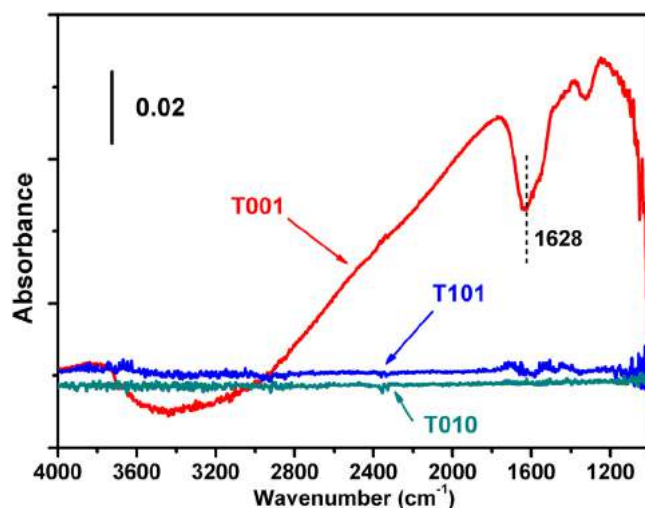


Fig. 7. IR spectra of T001, T101, and T010 after 5 min UV irradiation under N_2 atmosphere.

NH_3 . In addition, previous studies have reported that {001} facets exposed anatase TiO_2 favor to trap holes as oxidative sites while {101} facets incline to trap electrons as reductive sites by electron spin resonance (ESR) or single molecule fluorescence probe methods [29,30]. Since our DRIFTS are carried out at room temperature, the present characterization of photogenerated charges should be more appropriate than low temperature ESR technique.

3.3.2. The reaction mechanism for PCO of NH_3

We firstly investigated the role of O_2 in the PCO of NH_3 . On one hand, O_2 as an electron-capture to produce $\cdot\text{O}_2^-$, is beneficial to the separation of photogenerated e^- and h^+ ; on the other hand, O_2 can be an oxidant participating in the oxidation of substrate such as organic dyes. As shown in Fig. 8, NH_3 can be steadily removed

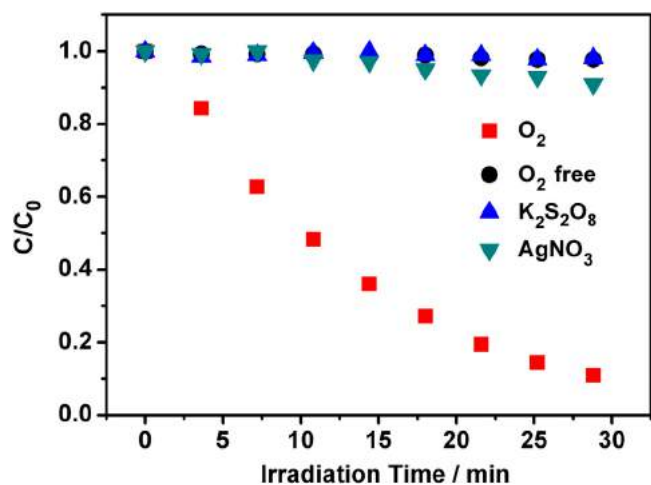


Fig. 8. Activity tests for photocatalytic oxidation of NH₃ in the presence of different electron-captures.

over T001 in the case of the co-existence presence of NH₃ and O₂. However, NH₃ was not oxidized in the absence of O₂ possibly due to the combination of photogenerated e⁻ and h⁺. When O₂ was replaced by AgNO₃ or K₂S₂O₈ which are common used electron-captures, still no activity of PCO of NH₃ was observed even though the photogenerated e⁻ and h⁺ are well separated. These results reveals that only efficient separation of photogenerated charges on the TiO₂ surface is not enough for realizing the NH₃ oxidation. As reported, the initial step of NH₃ oxidation is that the NH₃ is activated by a photogenerated hole to produce the amino radical ([•]NH₂) [46]. However, if O₂ does not participate in the subsequent oxidation of [•]NH₂, NH₃ oxidation would be terminated.

The reaction products of PCO of NH₃ in our flow system was also investigated. The products analysis on T001 (Fig. 9a) shows that no NO_x was detected and only 7 ppm N₂O were produced. Very recently, Raff et al. [47,48] reported that the oxidation of low concentration of NH₃ oxidation (ppb level) over TiO₂ will lead to the relative high yields of NO_x. Therefore, we deduced that the mechanism of high concentration of NH₃ oxidation might be different from the low concentration of NH₃ oxidation. We further analyzed the surface products over the T001 by TPD measurement after activity tests. As shown in Fig. 9b, a broad NO peak in the range of 250–340 °C and a weak NO₂ peak in the range of 150–300 °C appeared, which ascribe to the desorption of NO_x species (NO₂⁻ and NO₃⁻) formed over catalyst surface during the PCO of NH₃ [49]. Then it is indicated that NO_x is possibly the reactive intermediate products and then is active to be reactive with surface NH₂ to generate N₂.

Based on the above results, we propose that the reaction mechanism probably follows the photo-iSCR mechanism and is shown in Fig. 10. When TiO₂ is excited by UV irradiation, the electron-hole charge carriers are produced and then migrate to the surface of TiO₂ (step 1). Photogenerated holes initiate the NH₃ oxidation on the surface of TiO₂, which results in formation of the [•]NH₂ (step 2). In the following step (step 3), [•]NH₂ react with active oxygen species such as [•]O₂⁻ and [•]OH to generate the intermediate NO_x. Finally, the in situ formed NO_x is to be reduced by [•]NH₂ to produce N₂ or N₂O (step 4). The predominant {001} facets exposed TiO₂ has the higher hole migration compared with predominant {101} or {010} facets exposed TiO₂, then the kinetics rate of step 2 can be enhanced. Moreover, since the separation of photogenerated e⁻ and h⁺ is efficient over T001, more photogenerated e⁻ will be available to produce more active oxygen species, beneficial to step 3. Evidently, the T001 demonstrated the much high activity for the PCO of NH₃ oxidation (Fig. 4).

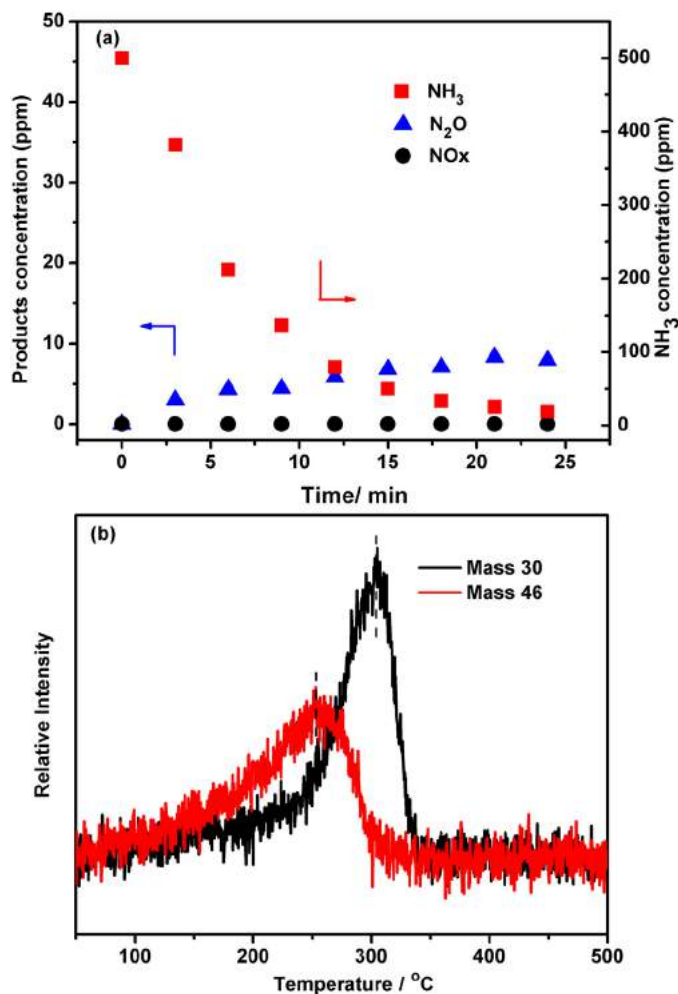


Fig. 9. Gaseous products analysis of photocatalytic oxidation of NH₃ on T001 (a). Surface products of NH₃ oxidation on T001 (b).

4. Conclusions

In summary, anatase TiO₂ nanoparticles with dominant {001}, {101}, and {010} facets exposed were successfully synthesized via the hydrothermal method. The photocatalytic activity order for NH₃ oxidation of is {001} > {101} > {010}. TiO₂ with dominant {001} facets allows more photogenerated holes to trap on its surface and therefore shows the highest efficiency for the separation of photogenerated electron-hole pairs among three catalysts. Since the photogenerated holes play a key role in the PCO of NH₃, the T001 showed much higher activity than T101 and T010. The photogenerated electrons could activate O₂ species and then participate in the formation of reactive intermediate NO_x followed by the photo-NH₃-iSCR to final products.

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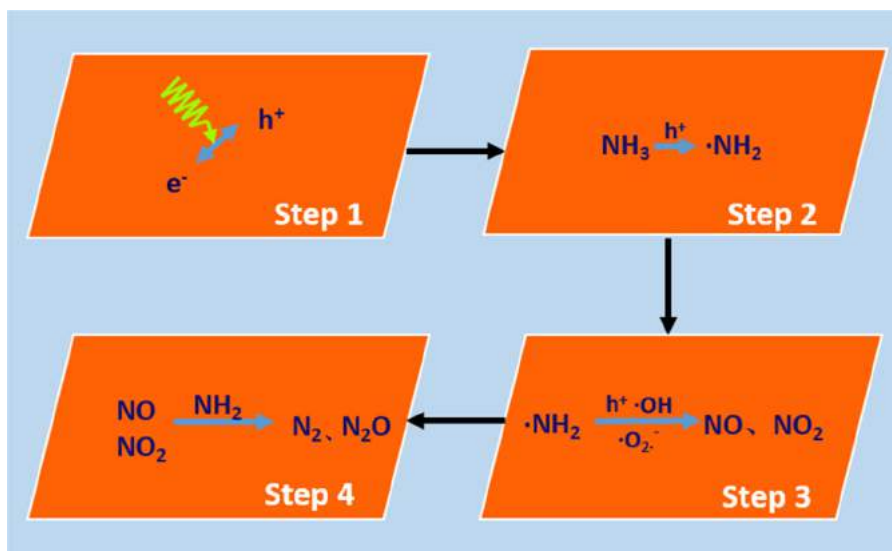


Fig. 10. Possible reaction mechanism of photocatalytic oxidation of NH_3 over TiO_2 .

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