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Surface Modification of (001) Facets Dominated TiO$_2$ with Ozone for Adsorption and Photocatalytic Degradation of Gaseous Toluene

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This study investigated the positive effect of surface modification with ozone on the photocatalytic performance of anatase TiO$_2$ with dominated (001) facets for toluene degradation. The performance of photocatalyst was tested on a homemade volatile organic compounds degradation system. The ozone modification, toluene adsorption and degradation mechanism were established by a combination of various characterization methods, in situ diffuse reflectance infrared Fourier transform spectroscopy, and density functional theory calculation. The surface modification with ozone can significantly enhance the photocatalytic degradation performance for toluene. The abundant unsaturated coordinated 5c-Ti sites on (001) facets act as the adsorption sites for ozone. The formed Ti-O bonds reacted with H$_2$O to generate a large amount of isolated Ti$_{5c}$-OH which act as the adsorption sites for toluene, and thus significantly increase the adsorption capacity for toluene. The outstanding photocatalytic performance of ozone-modified TiO$_2$ is due to its high adsorption ability for toluene and the abundant surface hydroxyl groups, which produce very reactive OH radicals under irradiation. Furthermore, the O$_2$ generated via ozone dissociation could combine with the photogenerated electrons to form superoxide radicals which are also conductive to the toluene degradation.

Key words: Ozone modification, (001) Facets, Toluene degradation, TiO$_2$, In situ diffuse reflectance infrared Fourier transform spectroscopy

I. INTRODUCTION

Volatile organic compounds (VOCs), such as aromatic, aliphatic hydrocarbons, and chlorinated hydrocarbons, are the major pollutants in indoor air and have serious environmental and health impacts. Photocatalytic oxidation (PCO) is one of the most active routes to eliminate most VOCs because it is cost-effective and environmentally friendly [1, 2]. TiO$_2$ is currently widely used in the field of degrading VOCs due to its low price, sensitive photoactivation, and high chemical stability [3, 4]. In the past decades, extensive efforts have been devoted to improving the performance of TiO$_2$-based photocatalysts using various methods, including surface modification [5, 6], metal ions (Ru, Ag, Au, and Pt) doping [7–9], non-metal ions (F, N, C, and S) doping [10–12], and coupling with a semiconductor such as CdS or SnO$_2$ [13, 14]. Mechanistic studies of VOCs degradation have been mainly focused on the adsorption sites, reaction mechanism, and kinetics [15, 16].

The adsorption of reactant on the surface of photocatalyst is the first crucial step for photo-degradation. Maira and Fresno et al. [17, 18] reported that the toluene was adsorbed on the TiO$_2$ via a $\pi$-electron-type interaction between aromatic ring and surface hydroxyl groups. Our previous work [19] also reported the similar results that toluene tends to be adsorbed on TiO$_2$ through three possible sites: the ortho-, meta-, and para-adsorption sites. Surface hydroxyl groups play a vital role in the toluene degradation. In addition to acting as the adsorption sites, the hydroxyl groups can also be transformed to very active OH radicals and are directly involved in the photocatalytic reaction by trapping photogenerated holes [20]. It is noteworthy that toluene adsorption sites include not only hydroxyl groups, but also oxygen vacancies and unsaturated surface Ti atoms [21, 22].

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Surface modification of TiO$_2$ is an effective approach to improve the photocatalytic performance [23–26]. For example, surface fluorination of TiO$_2$ not only traps the photogenerated electrons due to the high electronegativity of fluorine, but also favors the transformation of holes and promotes the production of surface hydroxyl radicals [6]. The TiO$_2$ modification via sulfation can promote the formation of surface sulfates, producing more hydroxyl groups than that of the pure TiO$_2$ and thus enhancing its degradation activity. We have investigated systematically the modification of TiO$_2$ with NH$_3$ and H$_2$S for the toluene degradation. The adsorption mechanism and relationship of surface structure-performance were established [19].

Facet engineering of semiconductor photocatalysts is a promising route to improve the photocatalytic performance [27]. Generally, the crystal facets with more undercoordinated atoms are more reactive in photocatalytic reactions. For example, the (001) facet of anatase TiO$_2$ contains 100% 5-fold coordinated Ti atoms in comparison to 50% 5c-Ti on the (101) facet, thus exhibiting higher photocatalytic performance [28]. Furthermore, for TiO$_2$, the photogenerated holes and electron can selectively migrate toward to (001) facets and (101) facets, forming an oxidation site and a suitable redox site, respectively [28]. In previous work [29], we found that the (001) facets of TiO$_2$ exhibit better toluene degradation activity than that of the (101) facets. The reason is that the (001) facets of TiO$_2$ provide a higher adsorption ability for toluene and molecular water.

Ozone has a high redox potential ($E_0 = 2.07$ V) and is widely used in the removal of organic and inorganic pollutants [30–32]. In the photocatalytic oxidation process, ozone is usually used as an additional oxidant to participate in the oxidation reaction [33, 34]. However, almost no relevant studies have been made to modify the surface of photocatalyst with ozone molecules. Based on previous studies [19, 29], we studied the adsorption and degradation process of toluene on (001) dominant TiO$_2$ modified by ozone in this work. Through various characterization techniques combined with in situ DRIFTS and DFT calculation, the modification mechanism of ozone and relationship of structure and performance were established.

II. EXPERIMENTS

A. Preparation of photocatalysts

TiO$_2$ with dominant (001) facet was prepared by a hydrothermal method [35, 36]. In a typical procedure, 9 mL of HF solution (40 wt%) as a shape-directing agent was first added into 30 mL of Ti(OC$_4$H$_9$)$_4$ under stirring for 30 min to make the solution homogeneous. HF should be handled carefully because it is highly corrosive. The mixture was then placed in a 100 mL autoclave and heated at 180 ℃ for 24 h. After naturally cooling down to ambient temperature, the obtained white precipitate was centrifuged and washed by ethanol and deionized water successively to remove residual organic matter and fluorine species completely, and finally dried at 80 ℃ for 24 h.

The ozone modification of the as-synthesized TiO$_2$ was performed on an ozone generator (PCE-22-LD, HeFei KeJing materials technology Co., Ltd.) equipped with a 200 W UV lamp. First, 0.01 g TiO$_2$ was dispersed in a moderate amount of deionized water, which was then uniformly coated on a glass substrate. After drying at 70 ℃ for 10 min, the sample was placed in ozone generator and radiated under the UV light. The obtained sample was denoted as O$_3$/TiO$_2$.

B. Characterization of photocatalysts

The powder X-ray diffraction (XRD) were performed on an instrument (TTRIII, Rigaku) with Cu Kα radiation. The catalyst morphology was tested by field emission scanning electron microscopy (FESEM, Sirion200, FEI), transmission electron microscopy (TEM, JEM-2011) and high-resolution transmission electron microscopy (HRTEM, JEM-2100F) equipped with a selected area electron diffraction (SAED). The percentage of exposed facets was estimated by Raman spectra (inVia, Renishaw). UV-Vis diffuse reflectance spectra (DRS) were measured using a LabRamHR spectrophotometer. The electron paramagnetic resonance (EPR) was measured on JES FA200 X-band spectrometer. X-ray photoelectron spectroscopy (XPS) data were recorded with a Thermo ESCALAB 250 XPS system using Al Kα (1486.6 eV) X-ray source.

C. Photocatalytic activity measurements

The catalytic performance for toluene degradation was tested on a home-made system, which consisted of a gas supply system, a 400 mL Pyrex glass photoreactor, and a gas chromatograph analytical system, as shown in FIG. S1 in supplementary materials. The light source was a 300 W Xe-arc lamp equipped with an IR-cutoff filter for eliminating the thermal effect (PLS-SXE 300UV, Beijing Perfectlight Technology Co., Ltd.).

In each experiment, the glass substrate coated with 0.01 g photocatalyst was placed into the photoreactor and 0.2 mL toluene was introduced into the photoreactor by injection. Before each reaction, the catalyst was first placed in the darkness for 0.5 h to achieve an adsorption/desorption equilibrium, and then illuminated by the Xe-arc lamp.

During the reaction, the concentrations of gaseous toluene were measured at an interval of 15 min with a GC (GC1690, Hangzhou Kexiao, China) equipped with a KX-112 column and a flame ionization detector (FID).
D. In situ DRIFTS test

The in situ DRIFTS experiments were tested in Shanghai Synchrotron Radiation Facility and the National Synchrotron Radiation Laboratory at University of Science and Technology of China.

A Nicolet 8700 FT-IR spectrometer equipped with a MCT detector was employed. The schematic diagram of the set-up is shown in FIG. S1 in supplementary materials). The reaction system consists of a DRIFTS accessory and a reaction cell (Harrick Scientific). The dome covering the sample cup has three windows: two ZnSe IR windows and one quartz window for introducing the irradiation light. The light source is monochromatic ultraviolet light (365 nm) with a power of 0.72 W (Honle, GBACS70-24-C14). In the experiment, the vapor of toluene was introduced into the reaction cell by dry air bubbling through the toluene solution.

III. RESULTS AND DISCUSSION

FIG. 1 (a) and (b) show the SEM and TEM images of the as-prepared TiO$_2$, which indicate that the TiO$_2$ particles have a regular nanosheet-like shape with a lateral size of about 100 nm×100 nm and a uniform thickness of ~10 nm (lower-left corner image in FIG. 1(a)). FIG. 1(c) shows a HRTEM image of the white pane area marked in FIG. 1(b). The two sets of mutually perpendicular grids with the same fringe spacing of 0.19 nm can be indexed to the (020) and (200) facets of TiO$_2$, which demonstrate that the rectangular facets are (001) facets. The well-defined SAED pattern in the inset of HRTEM image indicates that the as-prepared nanosheets have single-crystal structure. The HRTEM result clearly indicates that the TiO$_2$ nanosheets are exposed with (001) facet.

The XRD patterns of the pristine TiO$_2$ and ozone modified-TiO$_2$ are shown in FIG. 2. The diffraction patterns of both samples are indexed to the pure anatase TiO$_2$ (JCPDS No.21-1272). It is worth noting that the (004) peak is widened while (200) peak is sharp, indicating that the TiO$_2$ particles have a small grain size along the [001] direction and a large size along the [100] direction. The results further suggest that the as-prepared TiO$_2$ has a nanosheet-like structure, which is consistent with the SEM/TEM results. No obvious differences are observed between the XRD patterns of the pure TiO$_2$ and ozone modified sample, indicating that the crystalline phase of TiO$_2$ has not been changed by the surface modification of ozone.

FIG. S2 of supplementary materials shows the LRS of the pure TiO$_2$ and ozone modified-TiO$_2$. There are four peaks at the position of 141 cm$^{-1}$ ($E_g$), 634 cm$^{-1}$ ($E_g$), 393 cm$^{-1}$ ($B_{1g}$) and 515 cm$^{-1}$ ($A_{1g}$), respectively. The $E_g$ peak is related to the symmetric stretching vibration of O–Ti–O, while the $B_{1g}$ and $A_{1g}$ peaks are in connection with the symmetric and asymmetric bending vibration of O–Ti–O, respectively [37]. The (001) facet of TiO$_2$ contains only unsaturated 5c-Ti atoms and 2c-O bonding modes. This means that the symmetric stretching vibration modes of O–Ti–O is weak while the symmetric and asymmetric of O–Ti–O bending vibration is strong on the (001) facet. Generally, the percentage of (001) facets can be calculated based on the intensity ratio of $E_g$ to $A_{1g}$ peaks [38]. According to this, the percentages of (001) facet of the two samples were estimated to be 47% and 44%, respectively (Table S1 in supplementary materials). The results indicated that the as-prepared sample was dominated by (001) facet and ozone modification had no obvious impact on the percentage of (001) facet.

The optical absorbances of TiO$_2$ before and after ozonation modification were characterized by UV-Vis DRS. As shown in FIG. S3 (supplementary materials), both of the two samples exhibit a sharp absorbance in
FIG. 3 XPS spectra of (a) Ti 2p and (b) O 1s for TiO$_2$ and O$_3$/TiO$_2$.

the range of 300–400 nm$^{-1}$, and no obvious difference in their cut-off wavelengths is observed. The estimated band gap for the pure TiO$_2$ and ozone-modified TiO$_2$ are 3.0 eV and 3.02 eV respectively, which means that the band gaps of TiO$_2$ were not changed by ozonation treatment.

XPS spectrum was used to investigate the surface chemical environments of catalysts. Only Ti and O features were detected. No fluoride species were observed in the XPS spectra, indicating that fluoride species have been removed after the synthetic process. As shown in FIG. 3, two characteristic binding energies of Ti 2p$_{3/2}$ (458.9±0.1 eV) and Ti 2p$_{1/2}$ (464.7 eV) are observed in the two samples. The Ti$^{4+}$ is the main component in both samples, and ozonation has no obvious influence on the valence state and chemical environment of Ti atoms. The O 1s spectra of the pure TiO$_2$ show two characteristic binding energies at 530.12 eV and 531.25 eV, respectively. The former is assigned to O$^{2-}$ in the TiO$_2$ lattice, while the latter associates with the oxygen of the hydroxyl groups [34]. After ozone treatment, the binding energy of O$^{2-}$ in the TiO$_2$ remains almost unchanged. However, the peak position of oxygen in the hydroxyl groups is slightly shifted to lower binding energy (530.86 eV), suggesting a higher electron cloud density. Furthermore, it is noted that the area of peak increases significantly after ozone modification, indicating that the ozone modification leads to an increase in the amount of surface hydroxyl group.

To investigate the generation of active radicals in the catalysts during the photocatalytic reaction, the electron paramagnetic resonance (EPR) spin trapping technique was applied using DMPO as spin trap and the results are shown in FIG. 4. No EPR signal was detected when experiment was carried out in the dark or only DMPO was irradiated. In FIG. 4(a), a characteristic quadruplet with a signal-to-intensity ratio of 1:2:2:1 was observed, which demonstrated that both the samples produced OH$^-$ radicals during the photocatalytic reaction. The ozone-modified sample shows a much higher EPR signal intensity than that of the pure TiO$_2$, indicating that the ozone modification helps to produce more OH$^-$ active radicals, in agreement with the XPS result. From FIG. 4(b), the typical quadruplet with a signal-to-intensity ratio of 1:1:1:1 indicates that O$_2^-$ radicals were also generated in both samples under illumination. Similarly, the ozone-modified sample produced more O$_2^-$ radicals than that of the pure TiO$_2$.

The (001) facets of anatase TiO$_2$ contain a large amount of unsaturated coordinated Ti$_{3c}$ atoms, which have a strong Lewis acidity [39]. After ozone adsorbing on the strong Lewis Ti sites, it will be further distorted and unstable until a surface oxygen atom (Ti–O) and a free oxygen molecule are separated [39]. In order to understand the reaction mechanism, DFT was employed to investigate the reaction pathway of ozone adsorp-
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FIG. 4 DMPO spin-trapping EPR spectra for (a) DMPO-OH\(^{−}\) and (b) DMPO-O\(_2\)^{−} of TiO\(_2\) and O\(_3\)/TiO\(_2\) under UV irradiation.


The photocatalytic activity of the two photocatalysts for toluene elimination with the condition of room humidity 40% and initial toluene concentration of 100 ppmv were tested and the results are shown in FIG. 6. The photocatalyst treated with ozone exhibited a faster degradation rate for toluene than the pristine TiO\(_2\) without ozone modification, as shown in FIG. 6(a). The degradation rate of toluene increased with an increase in the ozone treatment time. The Langmuir-Hinshelwood model was employed to fit the degradation process using a reaction rate equation: \(\ln(C/C_0) = kt\). Here \(C_0\), \(C\), \(k\) and \(t\) represent the initial concentration of gaseous toluene, the final concentration of gaseous toluene after reaction, the corresponding first-order kinetic constant value and reaction time, respectively. From FIG. 6(b), the photocatalytic degradation reaction follows the pseudo-first-order kinetics, and the kinetic constant over the TiO\(_2\) treated with ozone for 8 h is 0.01535 min\(^{−1}\) and more than 2 times higher than that of the pristine sample (0.00693 min\(^{−1}\)). These results demon-
FIG. 6 (a) Photocatalytic degradation and (b) the kinetic constant values of gaseous toluene on TiO$_2$ with different ozonation time.

FIG. 7 DRIFTS spectra of pristine TiO$_2$ and O$_3$/TiO$_2$.

strate that the modification of TiO$_2$ with ozone has a positive effect on the photocatalytic toluene degradation.

In order to study the adsorption and degradation process of toluene on the ozone-modified sample, the \textit{in situ} DRIFTS was performed. FIG. 7 shows the DRIFTS of the fresh TiO$_2$ and O$_3$-modified TiO$_2$ samples. The narrow peak at 3693 cm$^{-1}$ corresponds to the isolated hydroxyl group on the surface of TiO$_2$ [42, 43], while the broad infrared absorption peak in the range of 3800–2600 cm$^{-1}$ is attributed to the $\nu_{\text{OH}}$ mode of the interacting hydroxyl group and symmetry and antisymmetric $\nu_{\text{OH}}$ mode superposition with Ti$^{2+}$ cation-coordinated water molecules [42]. It can be seen that the peak intensity of the isolated hydroxyl group at 3693 cm$^{-1}$ increased after ozone modification. The result indicated that the ozone modification promoted the formation of isolated hydroxyl group on the surface of TiO$_2$, which is consistent with the results of XPS and EPR aforementioned.

The \textit{in situ} DRIFTS for the adsorption of toluene on the two photocatalysts are shown in FIG. 8. With an increase of the adsorption time of toluene, the intensity of peak assigned to the isolated hydroxyl group (3693 cm$^{-1}$) decreased and almost completely disappeared after 15 min. The result indicated that the toluene was adsorbed on the isolated hydroxyl group on the catalyst surface. At the same time, a series of new absorption peaks are presented in the range of 3100–2850 cm$^{-1}$, which are assigned to the $\nu_\text{C-H}$ of aromatic ring (3083, 3046 and 3031 cm$^{-1}$) and the asymmetry and symmetry vibration of the methyl group C–H (2934 and 2884 cm$^{-1}$) [44]. The toluene has no obvious adsorption in the range of 2800–1800 cm$^{-1}$. The newly appearing peak at 1497 cm$^{-1}$ is attributed to the out-plane skeleton vibration of the aromatic ring, while the peak appearing at 1454 cm$^{-1}$ is related to the asymmetric bending vibration of CH$_3$ [44]. FIG. 9 compares the intensities of the characteristic IR peaks of toluene (3031 and 1497 cm$^{-1}$) adsorption on the surface of TiO$_2$ before and after ozone modification. Obviously, the ozone-modified TiO$_2$ shows a stronger IR peaks of toluene, indicating that the modification of ozone promoted the adsorption of toluene molecules on the TiO$_2$ surface. The reason can be attributed that the ozone treatment offers large amount of isolated hydroxyl groups on the (001) facets of TiO$_2$, which act as the adsorption sites for toluene molecules, as revealed by the DRIFTS results (FIG. 8).

After the adsorption toluene reached equilibrium, the samples were illuminated by UV lamp and the \textit{in situ} DRIFTS were recorded. As shown in FIG. 10, with increasing the illumination time, the intensity of broad peak at 3580 cm$^{-1}$ gradually decreased, and several new peaks (1638, 1603, 1581, 1498, 1456, 1416, 1320 and 1308 cm$^{-1}$) appeared in the range of 1800–1300 cm$^{-1}$. The absorption bands at 1638, 1603, and 1581 cm$^{-1}$ can be assigned to the benzaldehyde, and the bands of 1456, 1416 cm$^{-1}$ are related to the benzoic acid [45]. The band of 1498 cm$^{-1}$ is assigned to the in-plane skeletal vibration mode of aromatic ring [45], while the narrow bands at 1320 and 1308 cm$^{-1}$ correspond to the in-plane rocking vibration of CH$_3$ [46]. The benzaldehyde and benzoic acid are the key intermediates for the
Fig. 8 In situ DRIFTS spectra of toluene adsorption on (a) pristine TiO$_2$ and (b) O$_3$/TiO$_2$ photocatalysts.

Fig. 9 In situ DRIFTS spectra after toluene adsorption for 15 min on TiO$_2$ before and after ozonation.

toluene degradation. The toluene molecules were first oxidized to the intermediate benzaldehyde, and then further converted to benzoic acid under illumination, which is consistent with our previous study [19, 29]. Compared with pure TiO$_2$, it is noted that the ozone-modified TiO$_2$ shows a higher peak intensity ratio of benzaldehyde (1638, 1603, 1581 cm$^{-1}$) adsorption on the ozone-modified TiO$_2$, the results demonstrate that ozone-treated TiO$_2$ exhibited a faster rate of photocatalytic degradation of toluene than the pristine sample.

Reactive oxygen species (ROS), typically including hydroxyl radical (OH$^\cdot$), superoxide radical anion (O$_2^{-}$), singlet oxygen (O$_2$), and hydrogen peroxide (H$_2$O$_2$), have been considered as the main reactive species.
species for the photocatalytic degradation of VOCs [47]. Among these, the OH radicals show an extremely high oxidation ability and readily degrade various organic pollutants. Our previous study [29] proved that the (001) facets of TiO$_2$ are more active than the thermodynamically (101) facets for the toluene degradation. During the ozone treatment, the abundant unsaturated coordinated 5c-Ti sites on the (001) facets are likely to adsorb ozone molecule because of its strong Lewis acidity [39]. The characterization results indicate that the formed Ti–O bonds via ozone dissociation further reacted with H$_2$O to produce a large amount of isolated Ti$_{5c}$–OH on the surface, which act as the adsorption sites for toluene molecules, thus significantly promoting the adsorption of toluene on the surface of photocatalyst. Under irradiation, the generated very reactive OH radicals can rapidly degrade the toluene molecules. In addition, the O$_2$ produced via ozone dissociation can react with photogenerated electrons to form superoxide radicals (O$_2^-$), which are also the reactive species for toluene degradation. On the other hand, ozone molecule is electrophilic and may capture the electrons, thus promoting the separation of electron-hole pairs. All these factors are beneficial for the enhancement of photodegradation activity of ozone-modified TiO$_2$ with exposed (001) facets.

IV. CONCLUSION

In summary, we synthesized the (001) facets dominated TiO$_2$ nanosheets and investigated in detail the effect of ozone modification on the performance of the photocatalyst for photocatalytic degradation of toluene. The ozone-modified TiO$_2$ showed better performance for toluene degradation than the pure TiO$_2$. The detailed characterizations indicate that the ozone molecules were adsorbed on the abundant unsaturated coordinated 5c-Ti sites on (001) facets. The formed Ti–O bonds via ozone dissociation reacted with H$_2$O to produce a large amount of isolated Ti$_{5c}$–OH on the surface. The Ti$_{5c}$–OH act as the adsorption sites for toluene, thus significantly improving the adsorption ability of the TiO$_2$ for toluene. The enhanced performance of the ozone-modified TiO$_2$ is owing to its high adsorption ability for toluene and the abundant surface hydroxyl groups, which can produce very reactive OH radicals by trapping the photogenerated carriers. Furthermore, the produced O$_2$ via ozone dissociation can also combine with the photogenerated electrons to form super-
oxide radicals (O$_2^-$), which are also the reactive species for toluene degradation.

**Supplementary materials:** Schematic diagram of in situ DRIFTS setup for toluene adsorption, photoreactor, details of IR cell, Raman spectrum, UV-vis absorption spectrum and computational details.

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