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TiO₂ crystal facet-dependent antimony adsorption and photocatalytic oxidation

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ABSTRACT

Anatase TiO₂ crystal facets are garnering increasing attention due to their unique surface property. However, no specific linear relationship had been derived between the facet exposed on TiO₂ and the surface adsorption capacity as well as photocatalytic performance. This study systematically explored the facet effects on antimony (Sb) adsorption and photocatalytic oxidation using high-index {201} and low-index {101}, {001}, and {100} TiO₂. The results suggest that high-index {201} TiO₂ exhibits the best Sb(III) adsorption and photocatalytic activity compared to the low-index TiO₂. Both the Sb(III) adsorption density and the amount of ·OH and O₂^{·-} generated in solution were correlated to the magnitude of surface energy on TiO₂ facets. Photocatalytically generated ·OH and O₂^{·-} were responsible for Sb(III) photooxidation as evidenced by radical-trapping experiments. The great contribution of ·OH was observed only on {201}, not on low-index TiO₂. This phenomenon was found to be attributable to the high surface energy on {201}, which enables the generation of a large amount of photogenerated ·OH to compensate for the fast rate of ·OH dissipation. Therefore, the predominant participation of ·OH in Sb(III) photooxidation was only possible on high-index {201} TiO₂, which resulted in an enhanced photocatalytic rate. On the other hand, O₂^{·-} dominated the Sb(III) photocatalytic oxidation on low-index TiO₂. The intrinsic facet-dependent adsorption and photocatalytic mechanism obtained from this study would be useful for developing TiO₂-based environmental technologies.

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1. Introduction

TiO₂ crystal materials have been widely used as effective adsorption and photocatalytic media in environmental remediation [1,2]. Recent studies demonstrated that the adsorption and photocatalytic performance of TiO₂ largely depend on the crystal facets exposed and their corresponding surface energy [3–5]. The surface energy of low-index facets for anatase TiO₂ follows the order of {001} (0.90 J m⁻²) > {100} (0.53 J m⁻²) > {101} (0.44 J m⁻²), which is in agreement with its surface atomic structure and the density of under-coordinated Ti atoms [5]. As suggested by the previous studies [4–7], the adsorption affinity of molecules on TiO₂ basically depends on its surface energy. For example, water molecules [7,8], dye molecules [6,9], and Au clusters [10] could preferentially bind to {001} facet rather than {101} facet. Our previous study also showed that arsenic adsorption was more favourable on the high-energy {001} facet than on the thermodynamically stable {101} facet [11]. However, to the best of our knowledge, no specific linear relationship has been derived between adsorption capacity and facets exposed on TiO₂. Previous efforts at developing such a relationship were jeopardised because the experimental results using TiO₂ with mixed low-index facets would not allow a reliable theoretical calculation based on a specific facet. A cooperative approach of using TiO₂ with a specific crystal facet and a corresponding theoretical calculation method would be essential to successfully conduct such a study.

Facets exposed on TiO₂ play a pivotal role in the generation of reactive oxygen species (ROS) [11–13], such as the hydroxyl radical (·OH) and superoxide radical (O₂^{·-}), which are presumably the main oxidants in the TiO₂/UV photocatalytic processes [14–16]. Diverse evidence on this subject over the past decade highlights the intrinsic complexity of the facet effect on ROS generation and TiO₂ photocatalysis. For instance, TiO₂ with high-energy {001} facet has been reported to exhibit excellent photocatalytic performance by generating copious amounts of ·OH [17,18]. On the other hand, it was reported that the photocatalytic activity of the {100} facet in generating ·OH was three times higher than that of the {001} facet [12]. Further studies indicated that a higher ratio of {001} to {101} would not always lead to a higher photocatalytic activity; however, a delicate balance of low-energy {101} and high-energy {001} facets could synergistically enhance the photocatalytic performance of TiO₂ [19,20]. These outcomes emphasize the importance of the crystal facet-dependent photocatalytic mechanism in the design and implementation of TiO₂ for a wide spectrum of applications.

In theory, high-index facets should exhibit high chemical reactivity and surface energy due to the unique under-coordinated Ti surface structure. Recently, anatase TiO₂ tailored by high-index {201} facet was successfully synthesized, which has excellent electron storage and transfer properties [21]. TiO₂ {201} facet exhibits a high surface energy of 1.72 J m⁻² due to its specific surface atomic structure with under-coordinated Ti atoms. Thus, we used {201} facet as a model for high-index facet. We hypothesized that the high-index {201} TiO₂ should be a promising candidate for adsorption and photocatalysis.

The purpose of this study was, therefore, to examine the crystal facet-dependent adsorption and photocatalytic performance of TiO₂. To verify our hypothesis that high-index TiO₂ exhibits excellent performance, three low-index {101}, {001}, {100} TiO₂ samples and one high-index {201} TiO₂ were systematically investigated. Antimony (Sb), an analogue of arsenic, was selected as a probe molecule due to its wide-spread pollution and toxicity [22–24]. Also, the effect of TiO₂ facets on Sb adsorption and photooxidation is an uncharted area. The intrinsic facet-dependent reaction mechanism obtained from this study would be fundamental in develop-

ing TiO₂-based technologies. In addition, the mechanism of the facet dependence of adsorption and photocatalysis may be applicable to pollutant species other than antimony.

2. Materials and methods

2.1. Materials

Four types of TiO₂, including high-index {201} TiO₂, low-index {101}, {001}, and {100} TiO₂ samples, were synthesized and used in this study. The detailed synthesis method of TiO₂ with different facets is included in the [supplementary material](#). Tetrabutyl titanate (TBOT), terephthalic acid (TA), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), and superoxide dismutase (SOD) from bovine liver were purchased from Sigma-Aldrich (St. Louis, US). Isopropanol was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). An Sb(III) stock solution was prepared using KSB₄H₄O₇·1/2H₂O (Sinopharm, China). Deionized (DI) water was used to prepare all the solutions.

2.2. Characterization

The TiO₂ nanostructure was determined by X-ray diffraction (XRD) using a Bruker D8 X-ray powder diffractometer. The morphology of the samples was examined using a field emission scanning electron microscope (FE-SEM, SU-8000, Hitachi) with an acceleration voltage of 5.0 kV. The crystal morphology was characterized using a high resolution-transmission electron microscope (HRTEM, JEM-2100F from JEOL, Ltd.) with an acceleration voltage of 200 kV. The Brunauer-Emmett-Teller (BET) specific surface area was determined from the N₂ adsorption-desorption isotherms obtained using an automated gas sorption instrument (Quantachrome Instruments, US). The Sb concentration and speciation were determined using high performance liquid chromatograph (HPLC) coupled with a hydride generation-atomic fluorescence spectrometer (HG-AFS, Jitian, P.R. China). The detection limits for Sb(III) and Sb(V) are 1.3 µg L⁻¹ and 2.2 µg L⁻¹, respectively.

2.3. Sb(III) adsorption and photooxidation

Sb(III) adsorption and photooxidation experiments were conducted in an Erlenmeyer flask with 10 mg L⁻¹ Sb(III) in a suspension containing 0.2 g L⁻¹ TiO₂ and 0.04 M NaCl at pH 7. The samples were magnetically stirred in the dark for 4 h to achieve adsorption equilibrium before irradiation by a mercury UV lamp (CEL-M500, wavelength 275 nm) with an incident light intensity of 3950 µW cm⁻². A control experiment was performed in the dark. The photocatalytic process was monitored by taking 0.5 mL aliquots from the suspension at different irradiation time intervals. The samples were filtered through a 0.22-µm membrane before the HPLC-AFS analysis.

The adsorption capacity for Sb(III) in the dark was calculated according to Eq. (1):

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where q_e (mg g⁻¹) is the equilibrium adsorption capacity; C_0 and C_e (mg L⁻¹) are the initial and equilibrium Sb(III) concentration, respectively; V is the volume of solution (mL); and m is the mass (mg) of the adsorbent.

A first-order kinetic model was used to describe the photooxidation process according to Eq. (2):

$$\ln \frac{C}{C_0} = -kt \quad (2)$$

where C (mg L^{-1}) is the Sb(III) concentration at t min; C_0 (mg L^{-1}) is the Sb concentration before irradiation; k (min^{-1}) is the first-order kinetic rate constant and t (min) is the irradiation time.

2.4. ROS species determination

The measurement of $\cdot\text{OH}$ followed the procedure in a previous study [25]. Terephthalic acid (TA) was used as a fluorescence probe due to its reaction with $\cdot\text{OH}$ to generate 2-hydroxy terephthalic acid (TAOH), which emits a unique fluorescence band at around 426 nm. The suspension containing 0.2 g L^{-1} TiO_2 and 3 mM TA was magnetically stirred in the dark for 4 h to establish adsorption equilibrium. Then the sample was irradiated with UV light and 2 mL aliquots were taken at 15 min intervals with immediate filtration through a $0.22 \mu\text{m}$ PES membrane (Tianjin Jinteng Experiment Co., Ltd.) for fluorescence measurement. The photoluminescence (PL) emission spectra were recorded using a spectrofluorometer (Hitachi F-4500, Japan) with an excitation wavelength at 312 nm.

Online detection of $\text{O}_2^{\cdot-}$ generated during the UV irradiation in TiO_2 suspensions (0.2 g L^{-1}) was conducted using a continuous flow chemiluminescence (CFCL) apparatus as detailed in a previous report [26]. Luminol was selected as a chemiluminescence (CL) probe due to its selective detection of $\text{O}_2^{\cdot-}$; the CL signal was sensitive and not affected in the presence of TiO_2 .

The DMPO trapping electron spin resonance (ESR) signals were recorded on a Bruker EMX plus spectrometer with a 100 W mercury lamp (LOT-Oriel GmbH & Co. KG). The operation center field, microwave frequency, and power were set at 3503 G, 9054.6 MHz, and 0.998 mW, respectively.

2.5. Electrochemical impedance spectroscopy experiment

The electrochemical impedance spectroscopy (EIS) measurements were conducted to gauge the capacity of charge transfer using an electrochemical workstation (CHI 660D, Chenhua Instrument Co., China) in a standard three-electrode quartz cell. TiO_2 dip-coated Indium Tin Oxide (ITO) glass served as the working electrode ($1 \text{ cm} \times 2 \text{ cm}$ in size). Platinum wire was used as the counter electrode, and a Ag/AgCl (saturated in KCl) as the reference electrode. The EIS tests were conducted with an open-circuit potential by applying an AC voltage amplitude of 5 mV within the frequency range from 10^5 to 10^{-2} Hz in 0.04 M NaCl aqueous solution in the dark and under UV irradiation.

2.6. Computational details

Density-functional theory (DFT) calculations were conducted to examine the surface energy of different TiO_2 facets. The plane-wave based calculations were performed using the Castep package in Materials Studio (Accelrys, San Diego, CA). TiO_2 {201}, {101}, {001}, and {100} facets were cleaved from the optimized bulk anatase. A plane-wave cutoff energy of 340 eV was selected and the core electrons were treated using ultrasoft pseudopotentials. The generalized gradient approximation (GGA) approach of Perdew-Burke-Ernzerhof (PBE) was employed to calculate the exchange-correlation energy. The geometry optimization was calculated with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method until meeting the convergence criteria, 1.0×10^{-6} and 1.0×10^{-5} eV/atom, respectively, for self-consistent field (SCF) and energy tolerances [11,27].

3. Results and discussion

3.1. Morphological and structural properties of TiO_2

Fig. 1 summarizes the information on morphology of TiO_2 facets of the four types of TiO_2 crystal particles prepared in the present study. The information presented in Fig. 1 clearly shows that each of the four types of TiO_2 particles possessed predominantly a unique facet. (1) in Fig. 1a, the SEM image shows that the sample was composed of needle-like subunits pointing radially outward, forming a dandelion-like hierarchical structure [21]. Compared to Fig. 1a, the TEM images of Fig. 1b–c show a bundle of subunits with the measured lattice spacing of 2.4 Å for the presence of the {201} facet [21]. (2) in Fig. 1e–g, the TEM images show a characteristic lattice spacing of 3.5 Å for exposure of {101} facets and a particle size around 150 nm [19]. (3) in Fig. 1i–k, the SEM and TEM images show that the {001} TiO_2 had an average particle size of 40 nm with two sets of perpendicular lattice spacing of 1.9 Å corresponding to {001} facets [28,29]. (4) in Fig. 1m–o, the images indicate that the nanorod TiO_2 of about 750 nm was a tetragonal spindle with 80% exposure of {100} facets [30] and 20% of {101} facets observed on the tip of the spindle with a lattice spacing of 3.5 Å. A schematic description of the four types of TiO_2 crystals after the measured images has been provided in the last column in Fig. 1.

The XRD diffraction patterns reveal that all TiO_2 samples were in the anatase crystal phase as evidenced by the characteristic diffraction peaks for anatase crystal (Fig. S1a). The relatively high peak intensities indicate that they were also highly crystalline TiO_2 nanoparticles. The N_2 adsorption-desorption isotherms of the four TiO_2 materials are presented in Fig. S1b. The corresponding specific surface areas (S_{BET}) for each facet type of the TiO_2 particles were calculated according to its proportion over the whole surface. The S_{BET} for the four types of TiO_2 followed the order of {101} ($74.9 \text{ m}^2 \text{ g}^{-1}$) > {100} ($36.1 \text{ m}^2 \text{ g}^{-1}$) > {001} ($27.9 \text{ m}^2 \text{ g}^{-1}$) > {201} ($22.7 \text{ m}^2 \text{ g}^{-1}$). The difference in S_{BET} between the different TiO_2 particles may be attributable to the size and shape of these particles (see Fig. 1).

3.2. Sb(III) adsorption on the four TiO_2 facets

Sb(III) adsorption on the four TiO_2 nanoparticles was performed in the dark. The calculated adsorption capacity (q_e) for Sb(III) followed the order {201} (32 mg g^{-1}) > {001} (27 mg g^{-1}) > {100} (20 mg g^{-1}) > {101} (17 mg g^{-1}) (Fig. 2a). In general, adsorption capacity depends on available adsorption sites or S_{BET} . So, the normalized adsorption density of q_e by S_{BET} , $q_{e,n}$ (molecules/ nm^2), was calculated for comparison of the adsorption phenomena between the different TiO_2 facets. The results indicate that the normalized adsorption density $q_{e,n}$ obeyed the Langmuir model. Surprisingly, the normalized values $q_{e,n}$ for the different facet TiO_2 are very different, but followed the order of {201} (6.9) > {001} (4.7) > {100} (2.8) > {101} (1.1) (Fig. 2a). For example, the value of $q_{e,n}$ for {201} (6.9) is more than six times as much as that for {101} (1.1). This observation suggests that S_{BET} may not be the sole factor determining the Sb(III) adsorption capacity on TiO_2 , contrary to the common belief that adsorption capacity depends directly on S_{BET} [31]. The results here clearly indicate that, similar to arsenic adsorption on TiO_2 facets [11], the effect of TiO_2 crystal facets on Sb(III) adsorption is of great importance.

In order to find out if the unique adsorption property for the different TiO_2 facets is related to the surface energy, DFT calculations were conducted for the four TiO_2 facets. The surface energy

Fig. 1. FE-SEM (1st column), HR-TEM (2nd and 3rd columns) images, and schematic illustrations (4th column) for {201} (1st row), {101} (2nd row), {001} (3rd row), and {100} (4th row) TiO₂. Insets in the HR-TEM images show the measured lattice spacing.

Fig. 2. (a) Sb(III) adsorption capacity (q_e , blue) and BET normalized adsorption density ($q_{e,n}$, black) for TiO₂ {101}, {100}, {001}, and {201} facets. (b) Linear relationship between surface energy and the normalized adsorption density $q_{e,n}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Variation of Sb(III) concentration before and during UV irradiation, with and without the addition of scavengers (isopropanol for $\cdot\text{OH}$ and SOD for $\text{O}_2^{\cdot-}$) for the four type facets of TiO_2 (a) {201}, (b) {101}, (c) {001}, and (d) {100}. Initial Sb(III) = 10 mg L^{-1} ; $\text{TiO}_2 = 0.2 \text{ g L}^{-1}$; pH = 7.

calculated for four pure TiO_2 facets followed the order {201} (1.72 J m^{-2}) > {001} (0.96 J m^{-2}) > {100} (0.68 J m^{-2}) > {101} (0.49 J m^{-2}) (Fig. S2), which is also consistent with the previous study [32]. Similar to the calculation of S_{BET} for each facet type of TiO_2 , contributions from different facets have been taken into account in the surface energy calculation. The results reveal that the BET normalized adsorption density $q_{\text{e,n}}$ exhibited a linear relationship ($R^2 = 0.90$) with surface energy (Fig. 2b) at the 95% confidence level. The linear dependence of adsorption density on surface energy reveal that TiO_2 with a high-index facet has higher adsorption capability for Sb(III).

3.3. Sb(III) photooxidation on TiO_2 facets

TiO_2 has been widely used as an effective adsorbent, as well as an excellent photocatalyst [5,33]. Fig. 3 presents the changes in Sb(III) concentration in solution in the presence of TiO_2 before and after the UV irradiation during the control experiments. Note that before onset of the UV light, the decrease of Sb(III) concentration in solution must have been attributable to TiO_2 adsorption, as discussed above. The experimental data obtained during UV irradiation were fitted with zero-, first- and second-order kinetic models (Fig. S4 and Table S1). The results show that Sb(III) oxidation on TiO_2 facets followed first-order kinetics ($R^2 > 0.92$), regardless of the types of facet. The rate constant, k , was in the order {201} (0.0913 min^{-1}) > {101} (0.0231 min^{-1}) > {001} (0.0216 min^{-1}) > {100} (0.0168 min^{-1}) (Table S2). In contrast, Sb(III) was not oxidized under UV irradiation in the absence of TiO_2 (Fig. S3). The control experiments indicate that Sb(III) oxidation was negligible under dark conditions, confirming that ROS generated in the UV/ TiO_2 system were responsible for the Sb(III) oxidation. With the knowledge of the relative reaction rate constants obtained above for the four different types of facets, it would be interesting to examine how the production of ROS in solution would be different for these facets.

3.4. Identification of ROS in the Sb(III)- TiO_2 /UV system

ROS, such as $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$, were reported to be responsible for Sb(III) oxidation in the TiO_2 /UV system (Table 1) [24,34–37]. To evaluate the relative importance between $\cdot\text{OH}$ or $\text{O}_2^{\cdot-}$ for Sb(III) oxidation on the four TiO_2 facets, the radical trapping technique has been used with certain selective radical scavengers. The scavengers used here included isopropanol (220 mM) for $\cdot\text{OH}$ [38,39] and SOD (0.2 g L^{-1}) for $\text{O}_2^{\cdot-}$ [40]. The experimental results with the two scavengers are also presented in Fig. 3; the rate constants are tabulated in Table S2. The results of the reaction rate constants indicated that oxidation rate of Sb(III) on {201} TiO_2 had been suppressed by 69% and 59%, respectively after addition of isopropanol and SOD. In addition, Sb(III) oxidation on {001} TiO_2 had been reduced by 18% and 46% in the presence of isopropanol and SOD. In contrast, no influence had been observed in the Sb(III) oxidation by the addition of isopropanol to remove in solutions the $\cdot\text{OH}$ radicals for both {100} TiO_2 and {101} TiO_2 . Surprisingly, addition of SOD almost completely inhibited Sb(III) photooxidation for {100} TiO_2 (Fig. 3 and Table S1). These observations indicate that, both $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ played a role in Sb(III) oxidation for {201} and {001} TiO_2 . In comparison, superoxide $\text{O}_2^{\cdot-}$ radical species played a large role in Sb(III) oxidation for {101} and {001} TiO_2 and dominated the Sb(III)

Table 1
Chemical reactions and corresponding rate constants in Sb(III) oxidation.

Reaction	Rate constants (s^{-1}) or ($\text{M}^{-1} \text{s}^{-1}$)	Ref
1 $\text{TiO}_2 + h\nu \rightarrow e^- + h^+$		
2 $\text{H}_2\text{O} + h^+ \rightarrow \text{H}^+ + \cdot\text{OH}$		
3 $\text{Sb(III)} + \cdot\text{OH} \rightarrow \text{Sb(IV)}$	8×10^9	[35]
4 $\text{Sb(IV)} + \text{O}_2 \rightarrow \text{Sb(V)} + \text{O}_2^{\cdot-}$	1.1×10^9	[35]
5 $\text{O}_2 + e^- \rightarrow \text{O}_2^{\cdot-}$		
6 $\text{O}_2^{\cdot-} + \text{H}^+ \rightarrow \text{HO}_2$	1×10^{12}	[36]
7 $\text{HO}_2 + \text{O}_2^{\cdot-} + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	9.7×10^7	[36]
8 $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	8.3×10^5	[36]
9 $\text{Sb(III)} + \text{H}_2\text{O}_2 \rightarrow \text{Sb(IV)}$		[37]
10 $\text{Sb(IV)} + \text{O}_2 \rightarrow \text{Sb(V)} + \text{O}_2^{\cdot-}$	1.1×10^9	[35]

Fig. 4. Electron spin resonance spectra of radical adducts trapped by DMPO for (a) {201}, (b) {101}, (c) {001}, and (d) {100} TiO_2 dispersions under UV irradiation condition.

Fig. 5. Fluorescence spectra of 3 mM terephthalic acid solution mixed with the four types of TiO_2 under UV irradiation at different irradiation times: (a) {201}, (b) {101}, (c) {001}, and (d) {100} TiO_2 .

oxidation on {100} TiO_2 [41]. To elucidate further the role of the TiO_2 facets in creation of the radical oxidation species, further quantitative analysis of the radical species in relation to the specific facets was conducted.

ESR spectroscopy and fluorescence spectroscopy were employed to detect $\cdot\text{OH}$. The ESR spectra for the four types reaction systems are presented in Fig. 4. The characteristic spectra of $\cdot\text{OH}$ become clear after a few minutes of reaction time and the signal

intensity for {201} TiO₂ reaction system was the largest. Results from the fluorescence spectroscopy followed the same trend, indicating that signal intensity for ·OH was the highest for {201} TiO₂. The signal intensities for ·OH measured as function of time by fluorescence spectroscopy are presented in Fig. S5. All these results (Figs. 4 and 5 and S5) indicated that, the amount of ·OH produced in solution followed the order of {201} > {001} > {101} > {100} TiO₂, which is consistent with the photocatalytic oxidation rate of Sb(III) (Fig. S6a–b). Interestingly, a comparison of these results with those of reaction kinetics (Fig. 3 and Table S2) suggests that ·OH could only play a significant role when there was a certain large amount of it in solution during the photocatalytic process. For example, the Sb(III) oxidation on {201} TiO₂ was seen to be suppressed by 69%, where a higher concentration of ·OH radicals would exist (see Figs. 4 and 5), with the addition of isopropanol (·OH scavenger). However, no obvious suppression was observed in the Sb(III) oxi-

dation upon the removal of ·OH for {100} and {101} TiO₂ by the scavengers (Fig. 3), where relatively smaller amounts of ·OH were detected (Figs. 4 and 5). This demonstrated that, for the ·OH radical only at a high concentration could it produce a high oxidation reaction rate. By the way, it was also found that, although ·OH generated in solution has a short lifetime (200 μs) [42] it could build up a stable concentration under a constant UV irradiation condition.

The {201} TiO₂ produced a large quantity of ·OH radicals in solution because its needle-like subunits could readily facilitate the separation of photogenerated electron (e⁻) and hole (h⁺) pairs, which react with adsorbed H₂O and O₂ to generate ·OH and O₂⁻ (Table 1) [33]. The improved transfer of e⁻ and h⁺ can further be characterized with EIS experiments. Our results of the EIS experiments in Fig. 6 demonstrated that much an improved electric conductivity and a significantly reduced charge transfer resistance

Fig. 6. Electrochemical impedance spectroscopy of Sb(III) photooxidation on the four types of TiO₂ under conditions (a) dark and (b) irradiation. The initial Sb(III) concentration was 10 mg L⁻¹; TiO₂ was 0.2 g L⁻¹; the electrolyte solution was 0.04 M NaCl.

Fig. 7. Online detection of O₂⁻ generated in UV-irradiated Sb(III)-TiO₂ suspension. Red line represents the data for the Sb(III)-TiO₂ suspension; black line represents the data for the TiO₂ solution without Sb(III). The concentration of TiO₂ and luminol was 0.2 g L⁻¹ and 1 μM, respectively.

Fig. 8. Linear relationship of surface energy and (a) OH intensity, (b) O_2^- concentration.

existed on {201} TiO_2 as compared with other TiO_2 samples under UV irradiation. The convenient charge transfers in {201} TiO_2 would thereby retard the recombination of photogenerated e^- and h^+ and enhance the formation of ROS [21,43].

3.5. Quantitative analysis of O_2^-

Online detection of O_2^- generated in the four types of TiO_2 suspensions was performed by using a continuous flow chemiluminescence (CFCL) apparatus with luminol as the chemiluminescence probe [26]. The results are presented in Fig. 7. They show that without UV irradiation the concentration of O_2^- in solution of the four types of TiO_2 facets was negligible. Nevertheless, when the UV lamp was turned on, the O_2^- concentration increased significantly and reached an equilibrium value within 120–250 s. The concentration of O_2^- in the Sb(III)- TiO_2 systems was lower than that in TiO_2 alone suspensions, indicating the consumption of O_2^- in Sb(III) photocatalytic oxidation.

From the signal intensities detected (see Fig. 7), the amount of O_2^- followed the order {201} > {101} > {001} $\approx$ {100} TiO_2 , which is roughly in line with the order of Sb(III) photocatalytic oxidation rates under the corresponding reaction systems (Fig. S6c). However, further analysis indicated that only some fractions of the O_2^- generated on TiO_2 were consumed for the Sb(III) oxidation (Fig. S6d). Specifically, {201} TiO_2 generated totally 56 nmol L^{-1} O_2^- and 23 nmol L^{-1} was consumed during the reaction process, i.e., 41% of generated O_2^- was involved in the photocatalytic oxidation process. In comparison, {101} TiO_2 produced only 27 nmol L^{-1} O_2^- and 12 nmol L^{-1} (44%) was consumed during the reaction. However, for the {001} and {100} TiO_2 , only 21 nmol L^{-1} O_2^- was generated, which was all consumed during the photooxidation reaction. The difference observed in the fractions of O_2^- reacted in the four different TiO_2 systems appears to be attributable to the possible competition reactions between O_2^- and $\cdot\text{OH}$ in these systems. Both O_2^- and $\cdot\text{OH}$ played an important role in Sb(III) photocatalytic oxidation, where the effectiveness of $\cdot\text{OH}$ could only be pronounced as discussed before (Figs. 4 and 5 and S6). It may be possible that certain amounts of $\cdot\text{OH}$ generated in solution could not react during the photooxidation process due to its short lifetime (200 μs) compared to that of O_2^- (from 5 s up to hundreds of seconds) [42]. Nevertheless, the results in the present study and some of the previous studies show that, under a proper condition $\cdot\text{OH}$ radicals would substantially promote Sb(III) photooxidation rate likely due to its higher oxidant potential than that of O_2^- [44,45]. Finally, it was found that there appeared to exist a linear relationship between the surface energy and the amounts of $\cdot\text{OH}$ radicals as well as superoxide O_2^- , as summarized in Fig. 8 from the above experimental results.

4. Conclusions

This study explored the effects of TiO_2 crystal facet on Sb(III) adsorption and photocatalytic oxidation effectiveness. It has been found that the adsorption density and the amount of $\cdot\text{OH}$ and O_2^- generated in solution are correlated with the surface energy of the exposed crystal facets. TiO_2 {201} facet, likely due to a high surface energy ($\gamma = 1.72 \text{ J m}^{-2}$), exhibited the most effective Sb(III) adsorption capacity and photocatalytic oxidation performance, compared to the other three low-index TiO_2 facets, namely {101}, {100}, {001}. Both $\cdot\text{OH}$ and O_2^- were involved in the Sb(III) photocatalytic oxidation, but a significant reaction by $\cdot\text{OH}$ could only be observed when a large amount of $\cdot\text{OH}$ was generated. The formation of large amount of O_2^- and $\cdot\text{OH}$ on {201} TiO_2 appears to be attributable to the reduced charge transfer resistance, which retards the recombination of photogenerated e^- and h^+ and thus enhances the generation of ROS. The results obtained from the present study highlight the importance of crystal facets in adsorption and photocatalysis, which would shed some light on the design and application of TiO_2 -based materials.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2017.02.054>.

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