Journal of Colloid and Interface Science 496 (2017) 522–530

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

TiO_2 crystal facet-dependent antimony adsorption and photocatalytic oxidation

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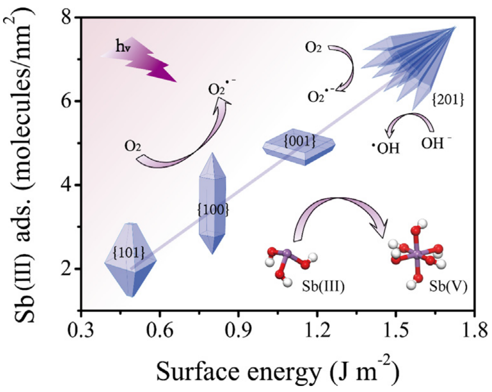
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 November 2016
Revised 20 February 2017
Accepted 22 February 2017
Available online 24 February 2017

Keywords:
TiO_2 facet
Surface energy
Reactive oxygen species
Radical trapping
$O_2^{\cdot-}$ online detection

ABSTRACT

Anatase TiO_2 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 TiO_2 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} TiO_2. The results suggest that high-index {201} TiO_2 exhibits the best Sb(III) adsorption and photocatalytic activity compared to the low-index TiO_2. Both the Sb(III) adsorption density and the amount of $^{\cdot}OH$ and $O_2^{\cdot-}$ generated in solution were correlated to the magnitude of surface energy on TiO_2 facets. Photocatalytically generated $^{\cdot}OH$ and $O_2^{\cdot-}$ were responsible for Sb(III) photooxidation as evidenced by radical-trapping experiments. The great contribution of $^{\cdot}OH$ was observed only on {201}, not on low-index TiO_2. This phenomenon was found to be attributable to the high surface energy on {201}, which enables the generation of a large amount of photogeneration $^{\cdot}OH$ to compensate for the fast rate of $^{\cdot}OH$ dissipation. Therefore, the predominant participation of $^{\cdot}OH$ in Sb(III) photooxidation was only possible on high-index {201} TiO_2, which resulted in an enhanced photocatalytic rate. On the other hand, $O_2^{\cdot-}$ dominated the Sb(III) photocatalytic oxidation on low-index TiO_2. The intrinsic facet-dependent adsorption and photocatalytic mechanism obtained from this study would be useful for developing TiO_2-based environmental technologies.

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http://dx.doi.org/10.1016/j.jcis.2017.02.054
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1. Introduction

TiO_2 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 TiO_2 largely depend on the crystal facets exposed and their corresponding surface energy [3–5]. The surface energy of low-index facets for anatase TiO_2 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 TiO_2 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 TiO_2. Previous efforts at developing such a relationship were jeopardised because the experimental results using TiO_2 with mixed low-index facets would not allow a reliable theoretical calculation based on a specific facet. A cooperative approach of using TiO_2 with a specific crystal facet and a corresponding theoretical calculation method would be essential to successfully conduct such a study.

Facets exposed on TiO_2 play a pivotal role in the generation of reactive oxygen species (ROS) [11–13], such as the hydroxyl radical ($^{\cdot}OH$) and superoxide radical ($O_2^{\cdot-}$), which are presumably the main oxidants in the TiO_2/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 TiO_2 photocatalysis. For instance, TiO_2 with high-energy {001} facet has been reported to exhibit excellent photocatalytic performance by generating copious amounts of $^{\cdot}OH$ [17,18]. On the other hand, it was reported that the photocatalytic activity of the {100} facet in generating $^{\cdot}OH$ 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 TiO_2 [19,20]. These outcomes emphasize the importance of the crystal facet-dependent photocatalytic mechanism in the design and implementation of TiO_2 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 TiO_2 tailored by high-index {201} facet was successfully synthesized, which has excellent electron storage and transfer properties [21]. TiO_2 {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} TiO_2 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 TiO_2. To verify our hypothesis that high-index TiO_2 exhibits excellent performance, three low-index {101}, {001}, {100} TiO_2 samples and one high-index {201} TiO_2 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 TiO_2 facets on Sb adsorption and photooxidation is an uncharted area. The intrinsic facet-dependent reaction mechanism obtained from this study would be fundamental in developing TiO_2-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 TiO_2, including high-index {201} TiO_2, low-index {101}, {001}, and {100} TiO_2 samples, were synthesized and used in this study. The detailed synthesis method of TiO_2 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 $KSbC_4H_4O_7{\cdot}1/2H_2O$ (Sinopharm, China). Deionized (DI) water was used to prepare all the solutions.

2.2. Characterization

The TiO_2 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 N_2 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 $1.3\ \mu g\ L^{-1}$ and $2.2\ \mu g\ L^{-1}$, 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 $0.2\ g\ L^{-1}$ TiO_2 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 $3950\ \mu W\ cm^{-2}$. 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):

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

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):

$$\ln\frac{C}{C_0} = -kt \tag{2}$$