Facet-dependent intermediate formation and reaction mechanism of photocatalytic removing hydrophobic anthracene under simulated solar irradiation

Weixiao Qi [a], Xiaoqiang An [a,*], Fan Zhang [a,d], Huijuan Liu [b,c], Jiuhui Qu [a,c]

[a] Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[c] University of Chinese Academy of Sciences, Beijing 100049, China
[d] Hebei University of Technology, Tianjin, China

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ABSTRACT

The intrinsic impact of inherent structures of facet photocatalysts on the reaction pathways and mechanism is largely unknown, although it is of scientific and technological importance for the research of water remediation. In this paper, hydrophobic anthracene (Ant) and TiO_2 with dominant $\{001\}$, $\{010\}$ and $\{101\}$ facets were selected as typical examples, to demonstrate the significant influence of exposed facets on the radical formation and intermediate production. The results showed that $\{101\}$ faceted TiO_2 showed superior catalytic activity than $\{001\}$ and $\{010\}$ faceted TiO_2 during the degradation of Ant under simulated solar irradiation, while $\{001\}$ faceted TiO_2 resulted in the largest production of anthraquione (AQ) intermediates. A fundamental study indicated that holes and oxygen played the important roles in the first step of catalytic oxidation of Ant on $\{001\}$ and $\{010\}$ faceted TiO_2, while $^\bullet OH$ radical was the main species to degrade AQ. The electron spin resonance spectroscopy measurements showed that their different abilities for the *in-situ* formation of $^\bullet OH$ radicals led to the differences in the intermediate products and reaction pathways. This work provides new insights into the development of high-efficiency photocatalysts for pollutant elimination through crystal-facet tailoring.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a type of ubiquitously-existed pollutants in the environment [1–3]. They could derive from combustion of fossil fuels and wood, refuse burning, coke oven, pyrolysis, forest and agricultural fires [4,5]. PAHs have been largely noticed and studied due to their own potential teratogenicity, mutagenicity and carcinogenicity, and possible derivation to more toxic product, such as nitro-PAHs (NPAHs) and oxy-PAHs (OPAHs) [6–10]. Due to hydrophobic and recalcitrant properties, PAHs and their derivatives are prone to adsorbing and accumulating around the interface of particulate matters. Thus, it is of great importance to eliminate PAHs pollutants in water through heterogeneous reactions. Among various techniques, photocatalysis has become one of the most attractive methods for

water remediation. The feasibility of catalyzed degradation of PAHs over photocatalysts has been investigated [11,12]. Unfortunately, their possible industrial application is limited by the moderate removal efficiency. In order to achieve high-efficiency photocatalysis, both new material strategy and fundamental understanding of the degradation mechanism are highly desirable.

Recently, tremendous efforts have been made to improve photocatalytic properties of photocatalysts through facet modulation [13–20]. It is found that the exposure of specific crystal facets is beneficial for the formation of high-density atomic steps and unsaturated coordination sites, which can attribute to the superior photoactivity [21,22]. Especially, the spontaneous charge separation on different facets of facet semiconductors has aroused considerable interests on facet engineered photocatalysts [23,24]. However, the intrinsic relation between facet control and pollutant degradation is still an open question. Take TiO_2 as an example, intensive research draw the conclusion that high-energy $\{001\}$ facets exhibit higher activity, because of the relatively higher surface energies in terms of computations [14,15]. In contrast, there

have been also discrepancies in the trends of crystal facet dependent photocatalytic activities. For example, Liu and co-workers found that photoreactivity of clean anatase facets follows the order of {001} < {101} < {010} [25]. Zhao et al. reported that anatase cuboids with dominant {100} facets exhibit 3 times higher photocatalytic activity in generating OH radicals than anatase sheets with dominant {001} facets [26]. Pradhan et al. and Zheng et al. reported that synergetic effect between low-energy {101} and high-energy {001} facets resulted in significantly enhanced photocatalysis [27,28]. Clarifying the effect of inherent characteristics of facet semiconductors on the photocatalytic reactions is a challenging research topic, although it has immense scientific and technological values for the design of more efficient photocatalysts.

Based on recent results, several factors show significant influence on the interfacial reactions over facet photocatalysts, such as surface reconstruction, dipolar field and surface states, while the anisotropic molecule adsorption further complicates the actual results. Indeed, it was found the interaction between the reactants and TiO$_2$ nanosheets affected both the separation efficiency of the photogenerated charge carriers and band gap of TiO$_2$ [29]. Unfortunately, most research mainly focused on the controllable synthesis of facets photocatalysts, thereafter the influence of exposure percentage of facet semiconductors on the photoreactivities. The intrinsic relation between interfacial structures and micromechanism is seriously neglected [29]. It is a critical point to deliberate the significant impact of electronic structures on the formation of reactive radicals and the diversification of reaction intermediates, which is extremely important for improving the efficiency of TiO$_2$ through crystal-facet tailoring.

In this study, anthracene, one of the priority PAHs, was selected as the model pollutant to investigate the contribution of crystal facet engineering on the photodegradation pathways. The different photodegradation mechanism of anthracene over three dominant facets of TiO$_2$ (001, 010 and 101) was firstly determined by studying the formation of intermediates and reactive radicals. The influence of surface structures on the removal efficiency was evaluated. We hope this study could provide new insight into the design of high-efficiency TiO$_2$-based facet photocatalysts, for the degradation of typical hydrophobic pollutants.

2. Experimental

2.1. Synthesis and characterization

TiO$_2$ nanoparticles with {001}, {010}, and {101} dominant facets were prepared through a hydrothermal method reported by Li et al. [30]. In a typical experiment, {001}-TiO$_2$ was synthesized using titanium butoxide and hydrofluoric acid solution at 200 °C for 24 h. Fluorine ions was removed by soaking the products in 0.1 M NaOH solution. {010}-TiO$_2$ was prepared by dissolving commercial anatase TiO$_2$ powder (Alfa Aesar, 325 mesh, 99.6%) in 10 M NaOH solution and hydrothermally treated at 180 °C for 24 h. After filtration, washing and hydrochloric acid treatment, H$_2$TiO$_3$ nanotubes were converted into {010}-TiO$_2$ through another hydrothermal reaction at 170 °C. Two-step hydrothermal reactions were used to fabricate {101}-TiO$_2$. P25 TiO$_2$ was first hydrothermally treated with 17 M KOH at 110 °C for 20 h. The resulting powders were further hydrothermally treated with ultrapure water at 170 °C for 24 h.

The crystal structures of prepared TiO$_2$ were confirmed by an X-ray diffractometer (XRD, X'Pert PRO MPD, PANalytical, Netherland). The morphology of particles was examined by high resolution transmission electron microscopy (HRTEM, JEM-2100F, Hitachi, Japan). The optical absorption spectra of {001}, {010}, and {101}-TiO$_2$ were obtained by using ultraviolet-visible diffuse reflection spectrophotometer (UV-vis DRS, Cary 5000, Varian, USA). The Mott-schottky measurements were carried out using an electrochemical station (Interface 1000, Gamry, USA). Brunauer-Emmett-Teller (BET) surface areas were measured using nitrogen adsorption-desorption isotherm measurements at 77 K (ASAP2020HD88, Micromeritics, USA).

2.2. Photodegradation experiments

Preadsorption of anthracene onto TiO$_2$ particles was carried out as Wen's reported method [11] with little modification. TiO$_2$ particles (20 mg) were added into acetone and then ultrasonic dispersed for 10 min. Anthracene was added into the TiO$_2$ emulsion, then solvent was volatilized completely under the magnetically stir at room temperature. According to the amount of anthracene and TiO$_2$ added, the surface coverage (mol/g) could be calculated. After the completely volatilization of solvent, 200 mL ultrapure water was added into the anthracene/TiO$_2$ suspension and ultrasonicated for 1 min. Then the suspension was magnetically stirred for 1 h in the dark to establish the adsorption/desorption equilibrium. A 500 W xenon lamp was used to irradiate the suspension with the irradiation intensity of 100 mW/cm^2. The spectrum of the light source was shown in Fig. S1. At selected irradiation time intervals, 5 mL of liquids were taken out and extracted with methylene dichloride for three times. The extract of each sample was concentrated, solvent-exchanged, and concentrated to 1 mL under a gentle stream of nitrogen. The internal standard (2-fluorobiphenyl) was added to the samples prior to instrumental analysis. All the photodegradation experiments were repeated at least two times.

2.3. Instrument analysis

Anthracene and the intermediate products formed during the photooxidation processes were analyzed by gas chromatography/mass spectrometer (GC–MS, Agilent 6890 GC with 5895C mass selective detector). A DB-17MS fused silica capillary column (30 m length × 0.25 mm diameter × 0.25 μm film thickness) was used for the separation of each compound. Samples (1 μL) were injected in splitless mode. The carrier gas was helium at a rate of 1 mL/min. Injector and detector temperatures were both kept at 300 °C. The program procedure was as follows: 80 °C (held for 1 min), to 120 °C at a rate of 20 °C/min, and to 290 °C at 10 °C/min (held for 10 min). Further information about compound identification and quantification were described in Text S1.

The active radicals formed during the photodegradation processes were detected by a Bruker electro-spin resonance Spectrometer (ESR, A300-10/12, Bruker, German) with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as trapping reagent.

3. Results and discussion

3.1. Materials characterization

All of the XRD diffraction peaks in Fig. S2 can be well-indexed to anatase phase TiO$_2$, which confirmed the quality and purity of the prepared TiO$_2$. Representative HRTEM and SEM images of faceted TiO$_2$ nanocrystals in Figs. 1 and S3 show the octahedral, belt-like, and plate-like morphologies of the {101}, {010}, and {001}-TiO$_2$. The BET surface areas for {001}, {010} and {101}-TiO$_2$ were 10.3, 2.1, and 5.5 m^2/g, respectively. The sizes of all nanocrystals are between 50 and 100 nm according to HRTEM images (Fig. 1). The crystal size of the TiO$_2$ were also calculated with Scherrer Equation from XRD to be 68, 52, and 102 nm for {101}, {010}, and {001}-TiO$_2$, respectively (Table S1). In this case, mass transfer limitation could be speculated to be absence in this study [31].