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Optimization of defect distribution in photodegradation of air pollutants via SiO_2-shell-enhanced fluorine modification

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ABSTRACT

The distribution of bulk and surface defects significantly affects the separation and injection of photogenerated charge carriers. In this study, we provide a strategy of SiO_2-shell-enhanced F modification to optimize the distribution of bulk and surface defects. The effects of SiO_2 coating and F modification on the physical structure, the separation behavior of photogenerated charge carriers, and the photocatalytic activity of P25 were studied by transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, surface photovoltage spectroscopy, and toluene degradation experiments. Results showed that the removal rate of toluene over SiO_2-F-modified P25 was significantly higher than those over P25 and F modified P25. The SiO_2-shell-enhanced F modification simultaneously increased the content of surface Ti^{3+} and reduced the bulk defects, thereby enhancing the separation of charge carriers. Furthermore, F doped at surface exerted a strong catalytic effect on the removal of toluene, whereas F doped in lattice caused the recombination of photogenerated charge carriers. The SiO_2 coating and calcination treatment significantly increased the amount of F ions doped at TiO_2 surface and inhibited F doping in lattice.

1. Introduction

Photocatalysis is one of the most promising technologies for environmental pollution control, H_2 generation, and solar cells [1–4]. In recent years, photocatalytic technologies with TiO_2 as the major catalyst, such as degradation of volatile organic compounds (VOCs), were practically applied for environmental cleaning [5–7]. However, the related moderate photoactivity limits its practical application [8].

The photocatalytic process is simply divided into three steps, namely, generation of charge carriers (electrons and holes), migration from bulk to surface, and injection from catalyst to adsorbed species. The photogenerated electrons and holes easily recombine before being injected to an electron acceptor (e.g., O_2) and donor (e.g., organic species and hydroxyl), resulting in declined photoactivity. The photoactivity of a certain catalyst is mainly determined by the separation and injection efficiencies of charge carriers. A defect is the major site for recombination or injection of charge carriers, and its effect on catalyst photoactivity was theoretically or experimentally studied in many works [9–12]. Bulk defect is the major recombination center of charge carriers, and the effects of surface defects are highly complicated. Surface defects, such as Ti^{3+} and oxygen vacancy, increase the adsorption amount of O_2 or other reactants and thus enhance the injection of photogenerated electrons [13–15]. Surface defects are beneficial in constructing an electric field which drives photogenerated electrons and holes to separation toward the opposite direction in the near-surface region [16]. Surface defects also act as the recombination center of photogenerated charge carriers [17,18]. Generally, the photoactivity of a semiconductor catalyst decreases as the bulk defects increase, but it increases with surface defects in an appropriate scale. Several methods have been developed to control the amount of surface and bulk defects. Domen et al. created surface defects on $LaTiO_2N$ surface by using a brief aqua regia treatment to improve the photoactivity of the catalyst [19]. Chen et al. synthesized black TiO_2 by introducing a disorder in the surface region of TiO_2 through hydrogenation [20]. This material presents a large amount of sur-

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face defects and demonstrates excellent solar-driven photoactivity. Hydrogen thermal treatment, high energy particle bombardment, or thermal annealing under oxygen-depleted atmosphere was also used to create defects on catalyst surfaces [21,22]. However, surface oxygen vacancy is not stable and easily heals in the presence of O_2 and H_2O [10]. Several studies reported that F doping creates stable Ti^{3+} at the surface or subsurface and significantly enhances the photoactivity of catalysts [23–25]. The above methods efficiently increased surface defects but are unable to reduce the amount of bulk defects. Calcination at a relatively high temperature increases the crystallinity degree of catalysts and thus decreases the amount of bulk defects. Li et al. reported that the relative concentration ratio of surface to bulk defects of TiO_2 increases with the heating temperature, and the increased ratio of surface/bulk defects enhances photoactivity [26]. However, the calcination method also presents limitations. The absolute amount of surface defects is reduced during heating. Moreover, nanocrystals merge into larger ones as the heating temperature is increased, causing reduced surface area and unfavorable phase transformation. TiO_2 transforms from a relative high active phase (anatase) to a relative low active phase (rutile) at the temperature of >650 °C [27]. To our knowledge, few methods have been reported to optimize the distribution of surface and bulk defects without the above limitations.

In the current study, we proposed a SiO_2-shell-enhanced F modification strategy to simultaneously reduce bulk defects and increase surface defects of TiO_2 without reduction of surface area and unfavorable phase change. The effects of SiO_2 and F on physical properties, defect distribution, charge carrier separation behavior, and photoactivity were studied using high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), surface photovoltage spectroscopy (SPS), and toluene degradation experiments.

2. Materials and methods

2.1. Catalyst preparation

Degussa P25 was used as model of TiO_2. SiO_2 shell was coated onto P25 nanoparticles by using the classic Stöber method [28]. For a typical synthesis, 0.75 g of P25, 70 mL of deionized water, and 5 mL of concentrated ammonia solution (28 wt%, Aladdin Chemistry, China) were added into 280 mL of absolute ethyl alcohol (99.5%, Aladdin Chemistry, China). Afterward, the mixture underwent ultrasonication for 15 min. Tetraethyl orthosilicate (2.4 mL, 99%, Aladdin Chemistry, China) was added dropwise to the dispersion of P25 particles for 10 min under continuous stirring, and the mixture was stirred at 25 °C for 18 h. Subsequently, the solution was centrifuged. The obtained solid was dried at 60 °C in an oven and calcined at 700 °C in furnace for 30 min. The obtained material was named as P25@SiO_2. Partial P25@SiO_2 was added to the HF solution (7 wt%) and stirred for 48 h to remove the SiO_2 shell and dope F at the catalyst surface. The mass ratio of P25@SiO_2 to HF solution was set to 1:30 to produce excessive F ions (the mole ratio of F:(Ti + Si) > 8). The solid was then washed with deionized water to remove the extra HF on the surface and was dried at 60 °C. The obtained SiO_2-F-modified sample was named P25@-F. A control material (P25-F) was synthesized following the same process, except for SiO_2 coating and calcination.

2.2. Photocatalytic experiment

Detailed information about the setups for the photocatalytic experiments was reported in our previous work [6,7]. The setups consist of a gas chamber, reactor, and gas chromatography (GC, 9790II, Fuli instrument, China) equipped with two flame ionization detectors and a methane converter, as shown in Fig. S1. An air pump with flow rate of 1 L/min was applied to circulate the air between the reactor and gas chamber. Another air pump with flow rate of 150 mL/min was used to circulate the air between the GC and gas chamber. The total volume of the whole system was 21.4 L. A quartz tube was placed in a dark box and surrounded by four UV lamps (8 W, Philips, central emission wavelength of 254 nm; the secondary wave at 183 nm was filtered) to complete the photocatalytic reactor. Briefly, 20 ± 0.1 mg of the prepared sample was dispersed in 10 mL of ethanol and coated on the inner face of a quartz tube by rotating in an oven. All quartz tubes were dried at 60 °C for 4 h before use. Highly pure air mixed with 79% N_2 and 21% O_2 (99.999%) was used to replace the gas in the system before each measurement. The initial relative humidity (RH) in the system was adjusted to 50% and detected by a humidity meter (DT-616CT, CEM, china). Toluene (99.5%, Aladdin Chemistry, China) was injected into the gas chamber until the toluene concentration in the system reaches up to 22 mg/m^3. Afterward, the gas in the chamber was switched to the reactor while simultaneously turning on UV light. The concentrations of toluene in the gas chamber were automatically detected by GC every 8 min. All measurements were repeated thrice.

2.3. Characterization of catalysts

A N_2 adsorption/desorption isotherm was detected using an Autosorb-iQ2-MP Surface Area Analyzer (Quantachrome, USA). The crystal pattern and crystal size were measured by XRD (D8 Advance, Bruker, Germany) with Cu Kα radiation ($\Delta 2\theta = 0.02°$, $\lambda = 0.15406$ nm). The morphology of the prepared samples was observed through HRTEM (JEM-2100, JEOL, Japan) at an accelerating voltage of 200 kV. The valence of the surface elements of the samples was analyzed by XPS (PHI Quantera II, Japan) with Al-Kα as X-ray source. The pressure of the XPS system was set to 6×10^{-6} Pa before the test. Each XPS curve was calibrated by an adventitious carbon signal at 284.6 eV. The separation efficiency and transfer direction of photogenerated charge carriers were estimated by an assembled SPS system. The system consists of a xenon lamp (500 W, LSB-X500, Zolix, China), a monochromator (Omni-λ300, Zolix, China), a light chopper (SR540, Stanford Research Systems, USA), a photovoltaic cell, a lock-in amplifier (SR830, Stanford Research Systems, USA), and a computer (Fig. S2). The samples were contacted with an upper ITO glass and a Cu base in the photovoltaic cell. The light from the monochromator was chopped to 23 Hz, and the prepared samples were irradiated through the upper ITO glass. The scanned monochromatic light began at 500 nm and ended at 300 nm. The RH and temperature in the room where the SPS system is located were set constant at 50% and 25 °C, respectively. Other details of the SPS system were reported in our previous works [6,7].

3. Results and discussion

3.1. TEM measurement

The micromorphology of the prepared samples was observed using HRTEM. Fig. 1A shows that P25 consists of nanoparticles with an average size of approximately 23 nm. SiO_2 was successfully coated on the P25 particles and formed a uniform shell, as shown Fig. 1B. The thickness of the SiO_2 shell for P25@SiO_2 was approximately 19.3 nm. After the SiO_2 shell was etched with HF solution, the exposed inner TiO_2 nanoparticle, P25@-F, exhibited shape and size similar to those of P25 (average 24 nm, Fig. 1C). TiO_2 particles combined into larger ones, accompanied by crystal phase transformation from anatase to rutile as the heating temperature