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Acid-assisted hydrothermal synthesis of nanocrystalline TiO_2 from titanate nanotubes: Influence of acids on the photodegradation of gaseous toluene

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ABSTRACT

In order to efficiently remove volatile organic compounds (VOCs) from indoor air, one-dimensional titanate nanotubes (TiNTs) were hydrothermally treated to prepare TiO_2 nanocrystals with different crystalline phases, shapes and sizes. The influences of various acids such as CH_3COOH, HNO_3, HCl, HF and H_2SO_4 used in the treatment were separately compared to optimize the performance of the TiO_2 nanocrystals. Compared with the strong and corrosive inorganic acids, CH_3COOH was not only safer and more environmentally friendly, but also more efficient in promoting the photocatalytic activity of the obtained TiO_2. It was observed that the anatase TiO_2 synthesized in 15 mol/L CH_3COOH solution exhibited the highest photodegradation rate of gaseous toluene (94%), exceeding that of P25 (44%) by a factor of more than two. The improved photocatalytic activity was attributed to the small crystallite size and surface modification by CH_3COOH. The influence of relative humidity (20%–80%) on the performance of TiO_2 nanocrystals was also studied. The anatase TiO_2 synthesized in 15 mol/L CH_3COOH solution was more tolerant to moisture than the other TiO_2 nanocrystals and P25.

Introduction

Volatile organic compounds (VOCs) are important toxic organic pollutants in indoor air. They are often noxious or carcinogenic, either directly or indirectly, having adverse effects on human health at low concentrations (Missia et al., 2010; Ohura et al., 2009). As one of the most promising techniques for the removal of VOCs from air, heterogeneous photocatalysis can destroy a broad range of VOCs and even completely mineralize them into innocuous CO_2, H_2O and mineral acids (Fig. 1). TiO_2 is the most commonly used photocatalyst because of its wide band-gap energy, nontoxicity, chemical stability and low cost (Ao et al., 2003; Demeestere et al., 2007; Noguchi and Fujishima, 1998; Obee and Brown, 1995). However, the photocatalytic activity of TiO_2 must be enhanced from the point of view of practical use and industrialization. Therefore, much effort has been devoted to improving the photocatalytic activity of TiO_2 by controlling phase, size, shape and crystallinity (Han et al., 2012; Liu et al., 2010).

Since first reported by Kasuga et al. (1998), titanate nanotubes (TiNTs) have attracted much attention, due to their one-dimensional nanostructures and high surface-to-volume ratios (Zhou et al., 2010). Although the lifetime of trapped electrons in TiNTs is longer than that in TiO_2 nanoparticles (Tachikawa et al., 2006; Thorne et al., 2005), the photocatalytic activity of TiNTs was lower than that of TiO_2 nanoparticles such as commercial P25, because of the impurity and lower crystallinity of TiNTs (Liu et al., 2008; Ou et al., 2008). Thus, methods such as hydrothermal and annealing treatments have been employed to transform TiNTs into

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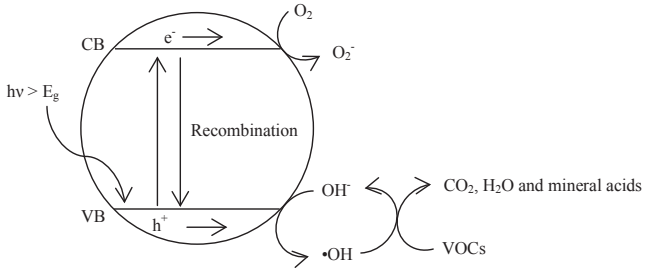

Fig. 1 – Schematic representation of photodegradation of gaseous toluene on TiO_2 surface.

TiO_2 nanocrystals to improve the purity and crystallinity, and consequently, the photocatalytic activity (Xu et al., 2012). Compared to annealing, hydrothermal treatment is a better method to prepare well-crystallized TiO_2 at relatively low temperatures (Yu et al., 2010; Zhu et al., 2011). Bavykin et al. (2011) reported that hydrothermal treatment of TiNTs with dilute H_2SO_4 solution (0.1 mol/L) resulted in their transformation into rutile TiO_2. High concentrations of HNO_3 (0.32–2.65 mol/L) also induced crystal transformation to rutile, while anatase forms were obtained in dilute HNO_3 solutions (0.01–0.1 mol/L) (Kim et al., 2012; Xu et al., 2010; Yu and Xu, 2007; Zhu et al., 2005). It was observed that anatase TiO_2 prepared in 0.05 mol/L HNO_3 solution showed higher photocatalytic activity toward gaseous acetaldehyde than P25 (Kim et al., 2012). Therefore, managing the phase transition of TiNTs could be of great use in the development of high activity TiO_2 and affected by the acid medium of hydrothermal treatment.

On the other hand, titanium precursors such as titanium alkoxides and inorganic titanium salts have been developed to prepare TiO_2 nanocrystals (Chen and Mao, 2007; Nakata and Fujishima, 2012; Patzke et al., 2011). The acid media used in the preparation have been observed to significantly influence the crystal structure and photocatalytic activity of TiO_2 nanocrystals (Nakata and Fujishima, 2012). It was observed that low concentration acids promoted the anatase form, *i.e.*, the most active phase of TiO_2 in photocatalytic processes, while high concentration acids promoted the rutile form (Tian et al., 2006; Wang et al., 2008; Wu et al., 2002). The ability of acids to promote anatase followed a sequence of $CH_3COOH > H_2SO_4 > HNO_3 > HCl$ (Wu et al., 2002). Ding et al. (2008) observed that anatase TiO_2 prepared in CH_3COOH solution exhibited a higher photodegradation rate toward methyl orange than that prepared in HCl solution. These results indicated that CH_3COOH seemed to be a promising choice to prepare highly efficient TiO_2 nanocrystals from TiNTs by promoting the phase transition to anatase. Moreover, CH_3COOH is safer and greener than strong oxidizing acids. However, as far as we know, the application of CH_3COOH as an acid medium for the phase transition of TiNTs, has not been examined.

In this study, therefore, in order to efficiently remove VOCs from indoor air, CH_3COOH was employed to synthesize nanocrystalline TiO_2 from TiNTs *via* the hydrothermal route. For comparison, various strong inorganic acid media, including HF, HCl, HNO_3 and H_2SO_4 were also investigated. The physicochemical properties of TiO_2 nanocrystals obtained under various acidic conditions were identified and related to their photocatalytic activities for the degradation of gaseous VOCs under UV irradiation. Toluene, which is one of the most common toxic organic pollutants in indoor air, was chosen as the target pollutant.

1. Experimental

1.1. Syntheses of titanate nanotubes and titania nanocrystals

The hydrothermal method initially developed by Kasuga et al. (1998) was employed for the synthesis of TiNTs. Briefly, one gram of commercial anatase TiO_2 (Aladdin Reagent Co., Ltd., China) was dispersed in 50 mL of 10 mol/L NaOH solution and hydrothermally reacted at 180 °C for 12 hr. The precipitate was washed with distilled water until the washing solution reached pH 7, and then dried at 50 °C. The tubes of TiNTs had an average outer diameter of 8 nm, an inner diameter of 6 nm and length of 100–200 nm (Fig. S1).

For acid-assisted hydrothermal treatment, 1 g of TiNTs was dispersed in 40 mL of an acid solution (either HF, HCl, HNO_3, H_2SO_4 or CH_3COOH). The concentrations of HF, HCl and HNO_3 were 0.015–1.5 mol/L, respectively. However, no solid product was obtained in 1.5 mol/L HF solution because of the dissolution of TiNTs in the solution by the reaction.

$$\text{Na-titanate} + HF \rightarrow TiF_6^{2-} + H_2O + Na^+ \quad (1)$$

The H_2SO_4 concentrations were 0.0075–0.75 mol/L. The concentrations of CH_3COOH were 0.015–15 mol/L. After thoroughly stirring, the mixtures were sealed in Teflon autoclaves and kept at 180 °C for 24 hr. The precipitates were washed with distilled water until the washing solution reached pH 7 and then dried at 50 °C. The TiO_2 powders were labeled as TX-a. For example, TiO_2 nanocrystals synthesized in 0.015 mol/L HNO_3 and 0.0075 mol/L H_2SO_4 solutions were denoted as $THNO_3$-0.015 and TH_2SO_4-0.015, respectively. The commercial P25 used for comparison was purchased from Degussa Corporation.

1.2. Characterizations

X-ray diffraction (XRD) patterns were collected between 20° and 90° (2θ range, Δ2θ = 0.02°) with a D/MAX 2550 PC using Cu *K*α radiation (Rigaku Corporation, Japan). The relative fractions of the crystal phases (anatase, rutile and brookite) and the average diameter of the crystallites, *d*, were calculated. Specific surface areas were determined in the range of relative pressure from 0.01 to 0.1, by N_2 adsorption experiments with the classical Brunauer–Emmett–Teller (BET) method using an Autosorb-1MP-VP surface area analyzer (Quantachrome Instrumments, USA.). Scanning electron micrographs (SEM) were obtained on an Utral 55 scanning electron microscope (CorlzeisD Corporation, German). Fourier transform infrared (FT-IR) spectra of TiO_2 nanocrystals synthesized in CH_3COOH were recorded in the wavenumber range from 1000 to 4000 cm^{-1} using a Nicolet 6700 FT-IR Spectrometer (Thermo Fisher Scientific Inc., USA). X-ray photoelectron spectroscopy (XPS) measurement of TiO_2 nanocrystals synthesized in HF was performed on a VG ESCALAB Mark II (Thermo VG Scientific Inc., UK) system with an energy resolution of 0.08 eV in a vacuum of 1.33×10^{-7} Pa, using a Mg *K*α X-ray source (1253.6 eV). All of the binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon.