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# One-dimensional titania nanotubes annealed at various temperatures for the photocatalytic degradation of low concentration gaseous pollutants

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## ABSTRACT

In this study, one-dimensional titania nanotubes (TNTs) were synthesized using a combined process of chemical and hydrothermal treatments, and their activities for the photocatalytic reactions of selected gaseous pollutants at sub-ppm levels were determined. Additionally, the properties of the TNTs were examined using selected spectroscopic methods. The annealed TNTs showed higher photocatalytic activities for the four target compounds than did the unannealed TNTs. For all the target compounds except benzene, the effect of the annealing temperature on the degradation efficiency was difficult to determine because all degradation efficiencies were very high. However, for benzene, which decomposed with a low efficiency, the degradation activities of the TNTs increased as the treatment temperature was increased from 250 to 300 °C, while they decreased slightly when the temperature was increased from 300 to 400 °C. These findings confirm the presence of an optimal annealing temperature for the synthesis of TNTs. Moreover, the average degradation extents for benzene, toluene, ethylbenzene, and *o*-xylene decreased from 92%, 96%, 99%, and 98% to 77%, 86%, 92%, and 94%, respectively, as the airstream flow rate increased within the range of 1–4 L/min. The average degradation extents decreased from 12%, 75%, 87%, and 88% to 3%, 29%, 46%, and 51%, respectively, as the input concentration increased from 0.4 to 1.9 ppm. Overall, these findings suggest that one-dimensional TNTs can be effectively utilized for the degradation of gaseous pollutants under optimal operational conditions.

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## Introduction

Advanced oxidation technology using semiconductors, defined as photocatalysis, has attracted much attention for the treatment of water and air pollutants (Adams & Impellitteri, 2009; Bernabeu et al., 2011; Destailats et al., 2012; Sánchez et al., 2012; Shi, Zhang, & Yao, 2011; Wu, Gao, Tu, Chen, & Zhang, 2010). Among the many semiconductor nanomaterials employed, titania (TiO<sub>2</sub>) has been widely used for gas- and liquid-phase pollution control, because of its potential oxidation capacity, high thermal stability, and low operational costs (Fujishima, Zhang, & Tryk, 2007; Nakata & Fujishima, 2012). Heterogeneous photocatalysis can be used to convert a wide range of toxic organic chemicals to harmless

compounds (i.e. carbon dioxide and water), through oxidation reactions involving OH radicals and O<sub>2</sub><sup>•−</sup> radicals. These radicals can be generated under UV irradiation at wavelengths corresponding to the band gaps of TiO<sub>2</sub> (i.e., 3.0 and 3.2 eV for rutile and anatase, respectively (Henderson, 2011)). However, the photocatalytic oxidation potential of the TiO<sub>2</sub> nanomaterial itself is limited by the recombination of electron–hole pairs produced under UV irradiation, these entities being closely associated with photocatalytic activity, because of charge-transfer effects (Mohamed & Bahnemann, 2012). It is necessary to lower the recombination of these photoinduced electron–hole pairs in order to improve the oxidation performance of TiO<sub>2</sub>.

Modification of the morphology of TiO<sub>2</sub> nanomaterials is a basic technique for improving TiO<sub>2</sub> oxidation performance by lowering electron–hole recombination effects. Hartmann, Lee, Smarsly, and Janek (2010) suggested that one-dimensional TiO<sub>2</sub> nanotubes (TNTs) would have lower electron–hole recombination effects than

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multidimensional TiO<sub>2</sub> nanoparticles owing to the free mobility of charge carriers throughout the length of the TNTs. In addition, these TNTs have a high specific surface area and multiple channels, which result in a high adsorption capacity and enhanced photocatalytic activity (Toledo-Antonio et al., 2007). These characteristics of one-dimensional TNTs have led to the multipurpose use of pure TNTs and other TNTs combined with metal or non-metal elements (e.g. silver, nitrogen, and phosphorus) as antibacterial agents. Applications have also been reported for chemical sensors, solar cells, and environmental treatment agents (Asapu et al., 2011; Lin, Rong, Ji, Fu, & Yuan, 2011; Toledo-Antonio et al., 2010; Ushiroda, Ruzyski, Lu, Spitler, & Parkinson, 2005). Furthermore, several research groups (Górska et al., 2008; Tachikawa, Tojo, Fujitsuka, Sekino, & Majima, 2006; Toledo-Antonio et al., 2010; Yu, Yu, & Cheng, 2007) have found that TNTs possess superior photocatalytic action to that of anatase TiO<sub>2</sub> nanoparticles for the photocatalytic oxidation of a variety of environmental pollutants, including aqueous phenol compounds, methyl orange, and reactive blue 69 dye.

To the best of our knowledge, the performance of TNTs for the photocatalytic degradation of volatile organic compounds (VOCs) at sub-ppm air levels has not been reported. Although Yu et al. (2007) applied TNTs to the photocatalytic degradation of gaseous acetone, they used a high feed concentration of 500 ppm, in contrast to the situation prevailing in many residential indoor environments where the concentrations of VOCs are at sub-ppm levels (<1 ppm) (Schlink, Thiem, Kohajda, Richter, & Strebel, 2010). The simple extrapolation of photocatalytic oxidation results obtained for contaminant levels at hundreds of ppm levels to much lower concentrations conditions is unlikely to produce valid results. Therefore, the current study was undertaken and investigated the applicability of photocatalysis for the removal of selected VOCs at sub-ppm levels using one-dimensional TNTs, synthesized through a combined process of chemical and hydrothermal treatments. It is well known that the proportion of anatase and rutile in TiO<sub>2</sub> can vary with the pretreatment temperature, thereby influencing photocatalytic activity (Sangchay, Sikong, & Kooptarnond, 2012). Therefore, in the present study, TNTs were treated at various temperatures to examine the relationship between photocatalytic activity and annealing temperature. The target compounds included four aromatic VOCs (benzene, toluene, ethylbenzene, and *o*-xylene (BTEX)), which were selected on the basis of their prevalence in residential indoor air (Schlink et al., 2010) and adverse health effects (Su, Jia, & Batterman, 2012).

## Materials and methods

### One-dimensional TiO<sub>2</sub> nanotubes

One-dimensional tubular-type photocatalysts were synthesized via a chemical-hydrothermal process. Briefly, pure TiO<sub>2</sub> powder (Aeroxide Degussa P25, Aerosil, Germany) with a 30% rutile and 70% anatase composition and an average particle diameter of ~32 nm was used as the TiO<sub>2</sub> source. 3.0 g TiO<sub>2</sub> was added to 130 ml 8 M KOH (≥85%, Sigma-Aldrich Inc., USA) solution and the mixture was hydrothermally treated at 160 °C in a 170 ml stainless steel autoclave for 20 h. The solid product was then recovered by filtration and cleaned with 0.1 M HCl and deionized water. The cleaned products were then conditioned in a vacuum oven at 80 °C for 12 h. The TNTs or pure TiO<sub>2</sub> powder were ground in an agate mortar and mixed with 2 ml of 0.1 M ethylenediaminetetraacetic acid (≥98.0%, Sigma-Aldrich Inc., USA) in preparation for coating onto the inner wall of the photocatalytic reactor. After the addition of 1 ml of distilled water to the mixture, 0.1 ml of Triton X-100 (10%,

Thermo Fisher Scientific Inc., USA) was added. Finally, the coated reactor was conditioned at 110 °C for 1 h and treated at various temperatures (250, 300, 350, or 400 °C) in an oven for 0.5 h.

The properties of the TNTs were investigated using a variety of spectroscopic methods. The morphological properties were examined using a Hitachi H-7600 transmission electron microscope (TEM), and X-ray diffraction (XRD) data were determined using a Rigaku D/MAX-RB X-ray diffractometer. Other structural properties of the samples were determined using a PerkinElmer Spectrum GX FTIR spectrophotometer. In addition, the surface area and porosity of the TNTs and powder-type P25 TiO<sub>2</sub> samples were examined using N<sub>2</sub> adsorption-desorption isotherms, obtained using a Micromeritics ASAP 2020 instrument.

### Photocatalytic activity tests

The photocatalytic activities of the TNTs for the oxidation of selected VOCs were investigated using a continuous-flow photocatalytic reactor consisting of a Pyrex tube with an i.d. of 4.5 cm and a length of 26.5 cm. The inner wall of the Pyrex reactor was coated with either the TNTs or the reference TiO<sub>2</sub> powder. A fluorescent daylight lamp with an annular shape, which allowed for uniform light distribution to be incident on the walls of the reactor, was inserted inside the reactor. The outside of the reactor was covered with aluminum foil to prevent light loss from the reactor lamp through the Pyrex reactor window and to block the influx of ambient light. The standard gas mixture was synthesized by injecting the liquid-phase target compounds into an evaporation stage using a syringe pump (KdScientific Model 210) and then mixing the resulting gas with flow-controlled humidified air. This airstream was flowed over the photocatalyst-coated Pyrex reactor. The humidity level was adjusted by allowing zero-grade air to pass through an activated charcoal filter, and then through water-containing Pyrex impingers held in a water bath. The relative humidity was monitored at both the inlet and outlet of the photocatalytic reactor using a humidity meter. The flow rate of the airstream was adjusted using flow meters and the flow determined using a mass-flow meter.

The photocatalytic degradation efficiencies of the TNTs were determined under various conditions and the variables studied included TNT annealing temperature, airstream flow rate, and input concentration. Four annealing temperatures (250, 300, 350, and 400 °C), four airstream flow rates (1, 2, 3, and 4 L/min), and five inlet concentrations (0.1, 0.4, 0.9, 1.4, and 1.9 ppm) were investigated. To test the effects of each parameter, the remaining parameters were fixed at the following values when not under investigation as a variable: annealing temperature: 300 °C, airstream flow rate: 1 L/min, and input concentration: 0.1 ppm. Visible-light radiation was provided by an 8 W fluorescent daylight lamp (F8T5DL, Youngwha Lamp Co.) with a spectrum of 400–720 nm and intensity of 2.0 mW/cm<sup>2</sup> at a distance from the visible-light lamp equal to half the hydraulic diameter (1.0 cm, defined as the i.d. of the annular reactor tube, minus the o.d. of the lamp) of the photocatalytic reactor. The light intensity was monitored using a Digital Lux Meter (Model DX-100, INS Instrument). The nominal coating areal density of the TNT photocatalyst was ~3.3 mg/cm<sup>2</sup>. A plug-flow reactor coated with pure TNT under the representative experimental conditions was also investigated for comparison purposes.

Air was sampled using an evacuated Tedlar bag at a constant flow rate, from which air was drawn through a sorbent trap containing Tenax TA (0.2 g) and Carboxen 569 (0.1 g). The sampling flow rates ranged between 0.1 and 0.3 L/min. The gas-phase compounds collected in the sorbent trap were analyzed using a thermal desorption system (Tekmar Model Aerotrap 6000) and a gas chromatograph (GC, Hewlett Packard 7890) fitted with a flame ionization detector. The quality-control program for the

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