Titania Nanotube for Degradation of Organic Vapors Under Different Conditions

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Abstract: In this study, carbon fiber sheet-supported titania nanotube (TNT) was prepared using a wetting-hydrolysis process. In addition, the photocatalytic activities of the prepared TNT for the decomposition of organic vapors under different operational conditions were investigated. The surface characteristics of the TNT were investigated using scanning electron microscopy, transmission electron microscopy, and X-ray diffraction. The average degradation efficiencies of benzene, toluene, ethyl benzene, and xylene decreased from 3–1%, 70–31%, 81–51%, and 82–50%, respectively, as the air flow rate increased from 1–4 L min^{-1}. Additionally, at an relative humidity of 20%, the average decomposition efficiencies of benzene, toluene, ethyl benzene, and xylene were 2, 69, 82, and 84%, respectively, while the values were ~1, 31, 67, and 75%, respectively, for an relative humidity of 90%. Consequently, it was suggested that three parameters (air flow rate and relative humidity) should be considered to maximize the photocatalytic activity of the prepared TNT photocatalyst.

Keywords: titania nanotube; organic vapor; flow rate; humidity; surface characteristic

Introduction

Heterogeneous photocatalysis over titanium dioxide (TiO_2) powder has been demonstrated to be an effective means for remediation of environmental pollutants [1]. This technique has the potential to oxidize a variety of organic pollutants to innoxious chemical species such as CO_2 and H_2O via reactions either with hydroxyl radicals or super-oxide ions [2,3]. However, photocatalytic oxidation activities of nanostructured TiO_2 powders have been often limited by the recombination effect of electron-hole pairs, which are formed when these powders are UV-light irradiated [3]. It is noteworthy that morphological characteristics of TiO_2 nanomaterials can result in different electron-hole recombination effects, which are closely associated with photocatalytic activity, owing to different charge transfer efficiencies. Certain research groups [4, 5] reported that

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electron-hole recombination effects could be reduced for TiO_2 nanotubes (TNTs) compared to nanostructured TiO_2 powders due to free movement of charge carriers over the full-length of nanotubes. Additionally, TNTs represented a high specific surface area as large as 425 m^2 g^{-1}, providing a high adsorption capacity that enhances their photocatalytic performance [6]. These features of TNTs have prompted to their multiple potential applications, including antibacterial agents, chemical sensors, and environmental pollutants purification [7–9]. Moreover, several researchers [4,8,10–12] reported superior photocatalytic performance of TNTs to that of anatase phase TiO_2 powders for the degradation of acetone, methyl orange, 4-(methylthio)phenyl methanol, phenol, or reactive blue 69.

Nevertheless, studies on TNT application for air pollutant treatments are rarely found in scientific literature. Accordingly, this study was conducted to examine the photocatalytic activity of TNT prepared using a wetting-hydrolysis process for the decomposition of organic vapors under different operational conditions. The target pollutants included benzene, toluene, ethyl benzene, and o-xylene, which were selected based on their high concentrations in residential and office buildings and their adverse health effects [13,14]. The organic vapors have well known indoor sources, such as building finishing materials, furnishings, household cleaning products, dry cleaning agents, paints, glues, cosmetics, textiles, and combustion sources [13]. In addition, these pollutants are known or suspected carcinogens, while some are associated with acute effects including liver and central nervous system [14]. These natures of organic vapors warrant the development of control means to minimize health risks.

Methods

Synthesis of TNT Photocatalyst

TNT was synthesized using a wetting-hydrolysis process with tetrabutyl titanate and carbon fiber sheet (CFS) as a Ti source and a supporting substrate, respectively. CFS (Hyundai Fiber Co.) was cleaned with 1 M NaOH solution (Sigma-Adrich) and with deionized water, after which it was dried in an oven at 100 °C. The cleaned CFS was immersed into tetrabutyl titanate (TBT, Sigma-Aldrich)-hexane (Sigma-Aldrich) solution (10 vol% TBT) for 20 min and then exposed to water-saturated air. These wetting and hydrolysis processes were repeated seven times to give high TiO_2 loading onto the CFS. The treated CFS was calcined in an oven at 350 °C for 8 h to give CFS-supported TNT. The surface characteristics of the TNT were investigated using scanning electron microscopy (FE-SEM, Hitachi S-4300), transmission electron microscopy (TEM, Hitachi H-7600), and X-ray diffraction (XRD, Rigaku D/max-2500 diffractometer).

Photocatalytic Activity Test

The photocatalytic system consisted of clean air supplying cylinder, humidification device, standard gas generator, and photocatalytic reactor. Clean dried air, which was supplied by a zero-grade air cylinder, was re-purified by passing through an activated carbon filter installed at the downstream air stream line. Subsequently, the clean dried air flowed to

water-containing impingers partially immersed in a temperature controlled water bath. The desired humidity was controlled by varying the ratio of humidified and dried air. The standard gas was synthesized by mixing humidified air with standard compounds injected into a Pyrex bulb via an automatic-programmed syringe pump (Model 510, KdScientific). The as-synthesized standard gas flowed through the annular region of the photocatalytic reactor. The photocatalytic reactor was prepared by coating the inner wall of an annular-geometry Pyrex tube (26.5 cm length and 5.0 cm inside diameter) with a thin film of S-TNT or pure TiO_2 (Degussa P25). A cylindrical visible-light source (8-W fluorescent day light lamp) was inserted into the Pyrex tube, which functioned as the inner surface of the photocatalytic reactor.

The photocatalytic activity of TNT was examined for photocatalytic degradation of the four organic vapors under different operational conditions by varying air flow rate (FR), input concentration (IC), and relative humidity (RH). The FR was adjusted at 1, 2, 3, or 4 L min^{-1} using rotameters, while the IC was fixed to 0.1 ppm. In addition, RH was adjusted at 20, 45, 70, or 90%. With respect to each parameter test, the other parameters were fixed to their representative values: FR, 1 L min^{-1} and RH, 45%. Air samples were collected by filling an evacuated 5 L Tedlar bag at a constant flow rate. The organic compounds were pretreated using a thermal desorption device (Perkin Elmer ATD 350) coupled to a mass spectrometer (Perkin Elmer Clarus SQ 8) (GC/MS) system using a fused silica column.

Results and Discussion

Characteristics of TNT

The surface characteristics of the CFS-supported TNT were investigated using spectral and optical analyses. As presented in Fig. 1, the SEM photograph of the prepared photocatalyst displayed the TNT arrays grown on CFS. In addition, the TEM images of the prepared photocatalyst demonstrated that the TNT had a nanotubular structure (Fig. 2). These findings demonstrate that the hydrothermal process used in this study can be utilized to grow TNT on the surface of the supporting substrate (CFS). Consistently, Fu *et al.* [15] observed that a nitrogen (N)-doped TiO_2 structure synthesized applying a solid-state reaction method with NH_4Cl as the N source had a tubular structure in its TEM image. Guo et al. [16] also reported that TiO_2 nano structures could be successfully prepared on CFS using another hydrothermal process.

Fig. 3 exhibits the XRD patterns of the CFS-supported TNT and the pure CFS. The XRD results of both the CFS-supported TNT and pure CFS demonstrated the presence of carbon, with a broad carbon-associated peak at $2\theta = 25.3°$, and a smaller C peak at $2\theta = 43.3°$. In addition, the CFS-supported TNT displayed a rutile crystal phase with a peak at $2\theta = 44.3°$ and an anatase crystal phase with a peak at $2\theta = 48.2°$, while the typical anatase peak at $2\theta = 25.3°$ was thought to be overlapped with the carbon peak of CFS. These results agree with those determined by Chen *et al.* [17].
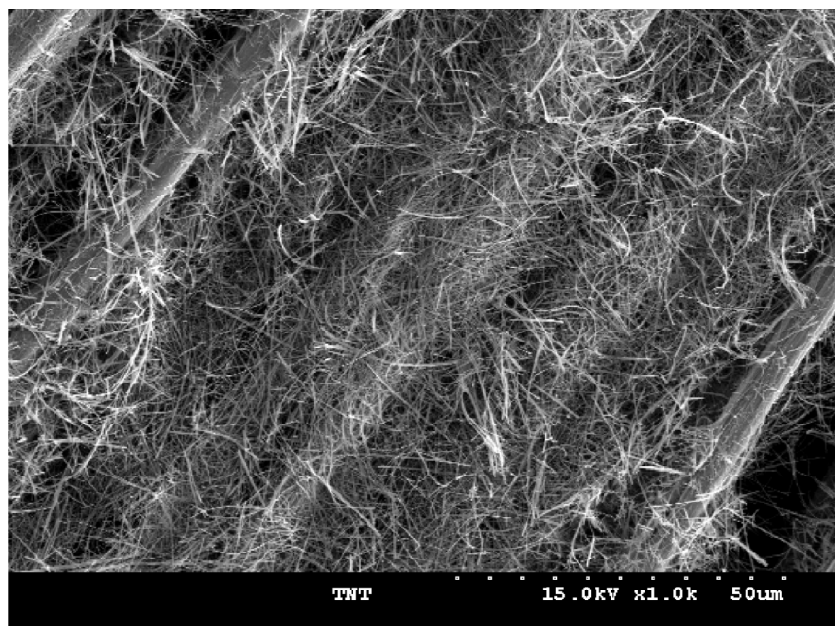
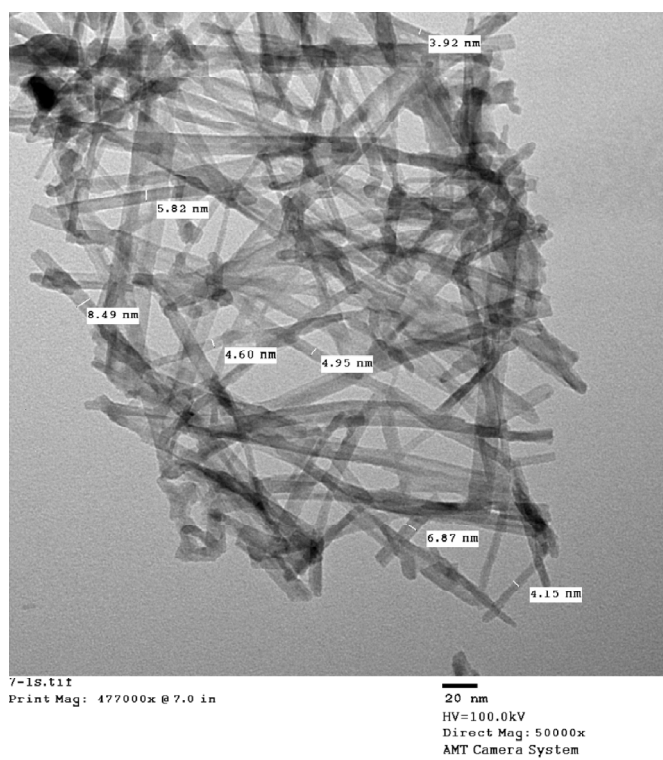**Figure 1:** Scanning electron microscopy of TNT

Figure 2: Transmission electron microscopy of TNT

Photocatalytic Activity of TNT

The time-series photocatalytic degradation efficiencies of BTEX determined using the prepared TNT according to FR are presented in Fig. 4. The BTEX degradation efficiencies displayed a decreasing pattern with increasing the FR. For instance, the average degradation efficiencies of BTEX decreased from 3 to 1%, 70 to 31%, 81 to 51%, and 82 to 50%, respectively, as the FR increased from 1–4 L min^{-1}. Consistently, Yu and Brouwers [18] observed a descending trend in NO degradation efficiencies when the FR was increased from 1–5 L min^{-1}. These results were attributed to the mass transfer of target compounds to the surface of the catalysts, and the reaction kinetics of target compounds, which are two important factors of heterogeneous photocatalytic degradation [19,20].

Fig. 5 shows the time-series degradation efficiencies of BTEX determined using the prepared TNT according to RH. The decomposition efficiencies of the target chemicals decreased as the RH increased. At an RH of 20%, the average decomposition efficiencies of BTEX were 2, 69, 82, and 84%, respectively, while the values were ~1, 31, 67, and 75%, respectively, for an RH of 90%. This pattern was consistent with that reported by Jeong et al [22] with respect to toluene determined using Degussa P25 TiO_2 under UV exposure. These results were ascribed either to the effects of the OH radical population or the competitive adsorption between water molecules and pollutants on the photocatalyst surface [22].
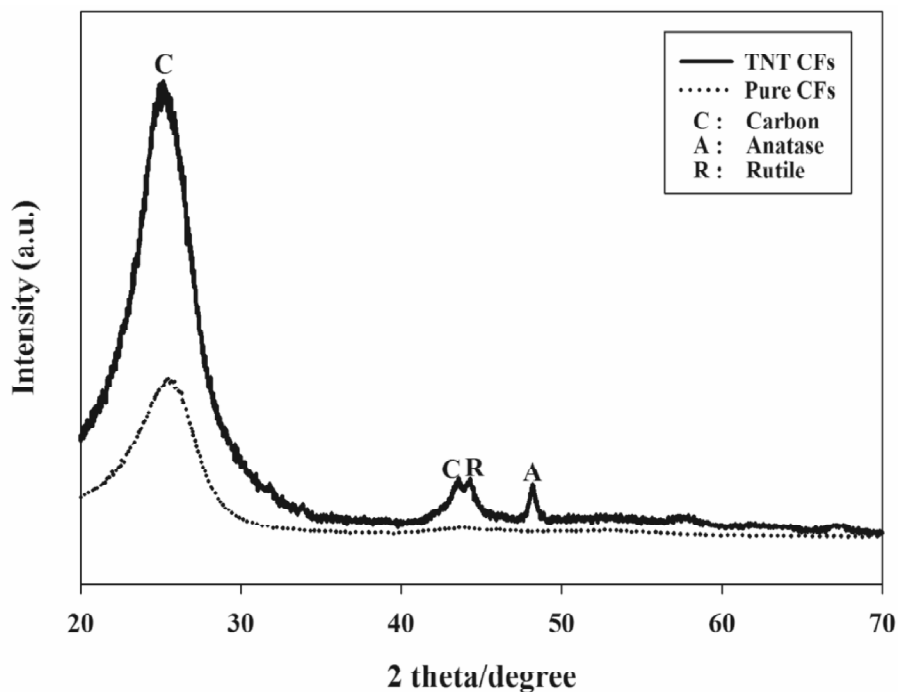

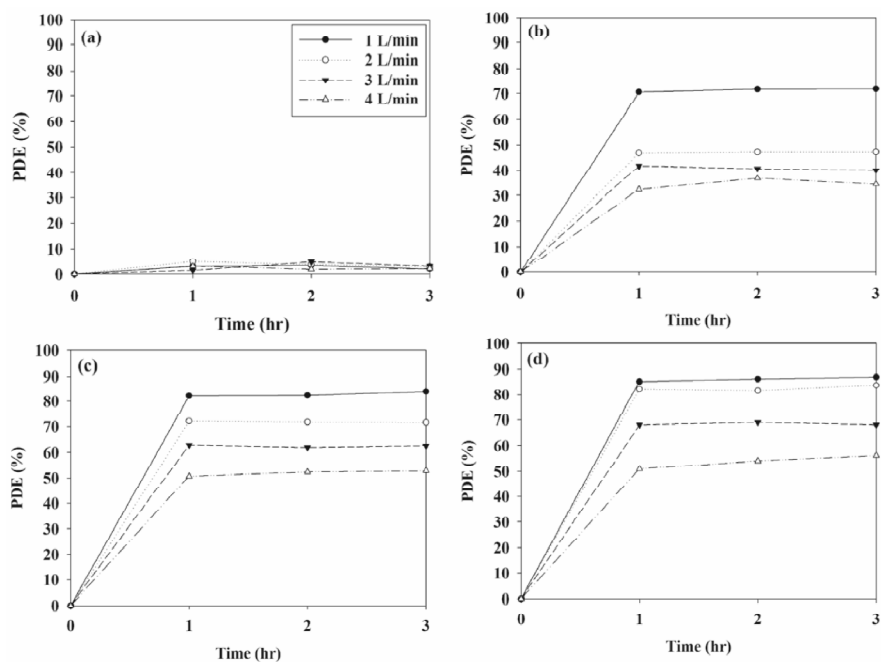**Figure 3:** X-ray diffraction pattern of TNT

Figure 4: Time-series photocatalytic decomposition efficiencies (PDEs) of (a) benzene, (b) toluene, (c) ethyl benzene, and (d) o-xylene as determined via TNT according to air flow rate
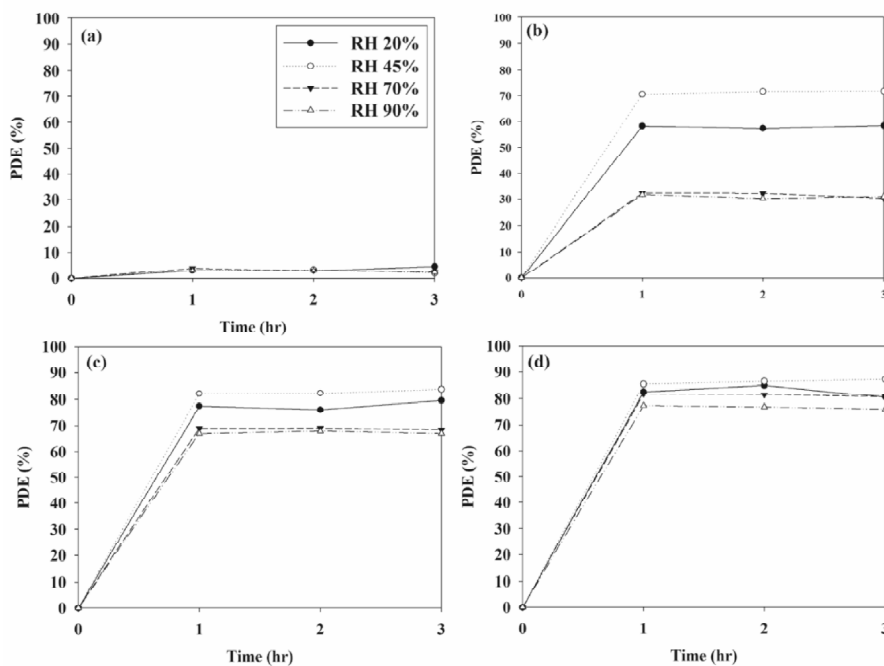

Figure 5: Time-series photocatalytic decomposition efficiencies (PDEs) of (a) benzene, (b) toluene, (c) ethyl benzene, and (d) o-xylene as determined via TNT according to relative humidity

Conclusion

This study was conducted to examine the photocatalytic activity of TNT prepared using a wetting-hydrolysis process for the decomposition of organic vapors. The spectral analyses of the prepared photocatalyst demonstrated that the SEM photograph of the prepared photocatalyst displayed the TNT arrays grown on CFS, and that the hydrothermal process used in this study can be utilized to grow TNT on the surface of the supporting substrate. In addition, it was suggested that two majo parameters (FR and RH) should be considered to maximize the photocatalytic activity of the prepared TNT photocatalyst.

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