Research Article

Feasibility of Carbonaceous Nanomaterial-Assisted Photocatalysts Calcined at Different Temperatures for Indoor Air Applications

Wan-Kuen Jo and Kun-Hwan Kim

Department of Environmental Engineering, Kyungpook National University, University Road, Bukgu, Daegu 702-701, Republic of Korea

Correspondence should be addressed to Wan-Kuen Jo, wkjo@knu.ac.kr

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This study examined the characteristics and photocatalytic activity of multiwall carbon nanotube-assisted TiO_2 (MWNT- TiO_2) nanocomposites calcined at different temperatures to assess their potential indoor air applications. It was confirmed that the composites calcined at low temperatures (300 and 400°C) contained TiO_2 nanoparticles bound intimately to the MWNT networks. Meanwhile, almost no MWNTs were observed when the calcination temperature was increased to 500 and 600°C. The MWNT- TiO_2 composites calcined at low temperatures showed higher photocatalytic decomposition efficiencies for aromatic hydrocarbons at indoor concentrations than those calcined at high temperatures. The mean efficiencies for benzene, toluene, ethyl benzene, and o-xylene (BTEX) by the composite calcined at 300°C were 32, 70, 79, and 79%, respectively, whereas they were 33, 71, 78, and 78% for the composite calcined at 400°C, respectively. In contrast, the efficiencies decreased to close to zero when the calcination temperature was increased to 600°C. Moreover, the MWNT- TiO_2 exhibited superior photocatalytic performance for the decomposition efficiencies compared to TiO_2 under conventional UV-lamp irradiations. Consequently, these carbonaceous nanomaterial-assisted photocatalysts can be applied effectively to indoor air applications depending upon the calcination temperature.

1. Introduction

The photocatalytic process using titanium dioxide (TiO_2) has become an attractive advanced oxidation technology for addressing a variety of environmental problems owing to its potential to oxidize a wide range of environmental pollutants and long-term thermodynamic stability under certain operating conditions [1, 2]. However, the current bottleneck for TiO_2 photocatalysis lies in its low quantum yield and low photodegradation efficiency. Therefore, a range of modifying methods were attempted to enhance the photocatalytic properties of TiO_2 for the decomposition of several environmental pollutants. The methods include nonmetallic doping, metallic doping, cocatalysts, dye sensitization, and adsorbent assistance [3–8].

Among these methods, carbonaceous adsorbent-assisted photocatalysts have attracted considerable attention because of their superior performance. Initially, granular- and fibrous-type activated carbons (ACs) were used as TiO_2 supporters for certain environmental applications [9–11]. Later, other types of carbonaceous nanomaterials (particularly carbon nanotubes (CNTs)) were suggested as alternative supporters of mainly TiO_2 due to the combined effect of the electronic and adsorption properties [7, 12, 13]. CNTs are generally classified into multi- and single-wall carbon nanotubes (MWNTs and SWNTs). The unique electronic properties of CNTs can retard the electron-hole recombination time, thereby enhancing the photocatalytic performance of TiO_2 [7, 13]. In addition, CNTs have the potential to provide reactive surface areas approaching those

provided by ACs and to adsorb hydrophobic species, which are barely adsorbed by TiO_2 nanoparticles [14]. Accordingly, many studies [15–19] applied MWNT- or SWNT-assisted TiO_2 photocatalysts (MWNT- or SWNT- TiO_2) for the purification of environmental pollutants and reported these nanomaterials to have superior performance to that of stand-alone TiO_2 . Unlike other types of photocatalysts, there are few reports on the effects of the calcination temperature of CNT-assisted TiO_2 photocatalysts on the gas-phase pollutant decomposition. In particular, the calcination temperature can be an important parameter associated with the photocatalytic activity for certain photocatalysts [20–24]. This suggests that the photocatalytic activity of CNT-assisted TiO_2 nanomaterials can vary with the calcination temperature.

Accordingly, this study examined the characteristics and heterogeneous photocatalytic activity of MWNT-assisted TiO_2 (MWNT- TiO_2) photocatalysts prepared at different calcination temperatures to assess the feasibility of their indoor air applications. Although SWNTs have a higher specific surface area, they are more expensive than MWNTs [25]. Therefore, this study used MWNTs as a cost-effective TiO_2 assistant material. The target environmental pollutants included four organic vapors (benzene, toluene, ethyl benzene, and xylene (also known as BTEX)), which are toxic or potentially toxic to humans [26]. These compounds are an important class of pollutants found frequently at high concentrations in a range of indoor environments [27]. The characteristics of BTEX have prompted the development of control means to minimize the health impacts of indoor air exposure. For indoor air applications, the surveyed concentration of each compound was chosen to be within the indoor air concentration (IAC) range (<1 ppm) [27].

2. Methods

2.1. Synthesis Route and Properties of MWNT-Assisted Photocatalyst. The MWNT- TiO_2 nanomaterials were synthesized using a sol-gel method. For this method, 0.7 g of MWNT (95.9%, Carbon Nano-material Technology) was added to 50 mL of ethanol (99.9% Merck) and sonicated for 20 min. Subsequently, 15.5 mL of tetrabutyl orthotitanate (TBOT, Sigma-Aldrich) was added to the MWNT-ethanol solution. This mixture was sonicated for 30 min to achieve better mixing and stirred vigorously for 30 min. Afterwards, 4 mL of nitric acid (69 wt%, Junsei) and 20 mL of deionized water were added to the solution to catalyze the hydrolysis and condensation. The resulting mixture was stirred vigorously until a homogeneous gel was formed. The gel was aged in air for 4 d at room temperature, crushed into fine powders, and dried at 80°C in an oven for 12 h. The powders were calcined at 300, 400, 500, or 600°C for 5 h. The calcined CNT- TiO_2 powders were coated on the inner surface of the pyrex reactor, using the method reported by Xagas et al. [28].

Before the coating procedure, the as-prepared MWNT- TiO_2 powders were examined for their surface and morphological properties. X-ray diffraction (XRD) patterns were determined on a Rigaku D/max-2500 diffractometer with Cu K_α radiation operated at 40 kV and 100 mA. Thermal

gravity analysis (TGA) was done using a TA Instrument SDT Q600 TG/DTA in order to determine the carbon content in the MWNT- TiO_2 powders. The particle morphology was observed using a Hitachi S-4300&EDX-350 FE-scanning electron microscope (SEM) at an acceleration voltage of 15 kV. X-ray photoelectron spectroscopy (XPS) measurements were done using a Thermo VG Scientific Escalab 250 spectrometer with monochromatized Al K α excitation. Fourier transform infrared (FTIR) analysis was performed on a PerkinElmer Spectrum GX spectrophotometer at a resolution of 4 cm^{-1} in the spectral range of 400–4,000 cm^{-1} , using a KBR pellet for sample preparation.

2.2. Application of MWNT-Assisted TiO_2 Nanocomposites to BTEX Decomposition. The experimental setup is illustrated in Figure 1. An annular-geometry reactor was used to evaluate the as-prepared MWNT- TiO_2 nanomaterials for the decomposition of gas-phase BTEX. The reactor consisted of a pyrex tube coated on the inner surface with a thin film of the MWNT- TiO_2 nanomaterials. A conventional cylindrical lamp or a hexahedral tube installed with light-emitting diodes (LEDs) was inserted inside another pyrex tube (outside diameter, 25 mm), whose outer surface served as the inner surface of the annular reactor. The gas flowed through the annular region. This design was particularly suited for research, because it provided a well-characterized reactive catalyst surface along the length of the reactor body and allowed uniform light distribution. Moreover, the reactor was designed to direct the flow of incoming air toward the UV light to increase the air turbulence inside the reactor, thereby enhancing the distribution of target compounds onto the catalytic surface of the reactor. The humidity was adjusted by passing zero-grade air through a charcoal filter, followed by a humidification device in a water bath. The relative humidity (RH) was measured in front of the photocatalytic reactor inlet using a humidity meter (T & D Thermo Recorder TR-72S). The flow rate (FR) measurement was carried out using identical rotameters (0–10 L min^{-1}) calibrated to a dry test meter (URG 3000-020C). The air stream was heated externally to help vaporize the BTEX injected into the mixing chamber through a syringe pump (Kd Scientific Model 210). The air stream was then finally fed to the photocatalytic reactor. The desired concentration of the standard gas was controlled by adjusting the FR and BTEX injection rate.

The major photocatalytic parameters were the input concentration (IC), RH, light source, FR, and hydraulic diameter (HD, which is defined as the inside diameter of the annular reactor tube minus the outside diameter of the lamp). The IC was fixed to 0.1 ppm for each component of BTEX to simulate the IAC condition. The RH was adjusted to 50%, which was within the American Society of Heating, Refrigerating and Air-Conditioning Engineers comfort range (40–60%). UV radiation was supplied using a conventional 8-W fluorescent black light (Sankyo Denki F8T5/BLB) with a maximum spectral intensity at 352 nm or 42 0.06-W UV-LEDs (Moksan MS-L512UVP) with a maximum spectral intensity at 380 nm. The FR was adjusted

FIGURE 1: Schematic diagram of the experimental setup.

FIGURE 2: X-ray diffraction pattern of MWNT-TiO₂ at four different calcination temperatures (300, 400, 500, and 600°C).

to 1.0 or 4.0 L min⁻¹, giving a residence time of 7.2 and 1.8 s, respectively. The former FR was used to compare the decomposition efficiencies of the MWNT-TiO₂ composites irradiated using the two light-source types. The latter FR was used to examine the effects of the calcination temperature on the photocatalytic decomposition efficiency of the nanocomposites. The HD of the reactor was 10 mm.

Air measurements were performed by collecting air samples periodically at the inlet and outlet of the photocatalytic reactor and analyzing them by gas chromatography (GC, Hewlett-Packard 4890) or mass spectrometry (MS, Hewlett Packard MSD5973) coupled with a thermal desorption (TD, Donam TD-II) unit. Sampling was done by filling an evacuated Tedlar bag at a constant flow rate. The gas from this bag was then drawn through a 0.64 cm outside diameter and 18 cm long SS sorbent trap containing 0.4 g of Tenax TA using a constant flow-sampling pump (SKC Aircheck Sampler Model 224-PCXR8). The sampling time was varied from one to five min depending on the flow

rate. All samples were taken at room temperature. The gaseous species collected on the sorbent trap were analyzed by TD/GC installed with a flame ionization detector or GC/MS. The quality control program involved an analysis of the laboratory blank traps and spiked samples. At the beginning of the day, a laboratory blank trap was analyzed for contamination but no trap contamination was identified. A spiked external standard was also analyzed daily to check the quantitative response. The method detection limits ranged from 0.3 to 0.5 ppb for BTEX, depending on the compounds.

3. Results and Discussion

3.1. Properties of MWNT-Assisted TiO₂ Nanocomposites according to Calcination Temperature. The characteristics of the MWNT-assisted nanomaterials prepared at different calcination temperatures were investigated using a range of optical and analytical instruments. Figure 2 exhibits the XRD patterns of the MWNT-TiO₂ composites calcined at four different temperatures (300, 400, 500, and 600°C, for MWNT-TiO₂-300, MWNT-TiO₂-400, MWNT-TiO₂-500, and MWNT-TiO₂-600, resp.). The anatase content of the composites decreased with increasing calcination temperature and the rutile and brookite contents increased. This pattern is consistent with that reported by Wang et al. [15]. In addition, the peak at 25.3° 2θ became broader with decreasing calcination temperature. The broad peaks obtained from both the MWNT-TiO₂-300 and MWNT-TiO₂-400 were assigned to overlap of the peak at 26.0° 2θ, which was assigned to MWNTs [14], with the anatase peak at 25.3° 2θ [29]. The sharp peaks at approximately 25.3° 2θ for both MWNT-TiO₂-500 and MWNT-TiO₂-600 were attributed to the low thermal stability of MWNTs [25]. MWNTs and certain unidentified chemical species might have been destroyed during the calcination processes under such high-temperature conditions. This assertion was supported by TGA (Figure 3), in that there were no significant weight losses for the MWNT-TiO₂-500 and MWNT-TiO₂-600. Consequently, TiO₂ crystallites would be

FIGURE 3: Thermogravimetric analysis of MWNT-TiO₂ at four different calcination temperatures (300, 400, 500, and 600°C).

the major component of these composites, resulting in sharp peaks at approximately $25.3^\circ 2\theta$.

Figure 3 also exhibits that for the MWNT-TiO₂-300 and MWNT-TiO₂-400, three-step weight losses were observed over the temperature range 20–800°C. An endothermic weight loss was observed between 20 and 500°C, which was attributed to the release of the residual TiO₂ precursor and organic solvent. A second sharper weight loss (11 and 2.4% for the MWNT-TiO₂-300 and MWNT-TiO₂-400, resp.) was observed between 500 and 600°C and attributed to the thermal decomposition of MWNTs and the crystallization of amorphous TiO₂ [14]. On the other hand, almost no weight loss was observed between 630 and 800°C, suggesting that TiO₂ became the major component at this temperature range.

Unlike the MWNT-TiO₂-300 and MWNT-TiO₂-400, SEM images revealed almost no MWNTs in MWNT-TiO₂-500 and MWNT-TiO₂-600 (Figure 4). This supports the assertion that MWNTs might have been destroyed during the calcination processes at high temperatures. In contrast, TiO₂ nanoparticles in MWNT-TiO₂-300 and MWNT-TiO₂-400 were bound intimately to the MWNT networks.

Figure 5 illustrates the XP spectra of the C 1s regions for the MWNT-TiO₂ composites calcined at four different temperatures. The spectra of the MWNT-TiO₂-300 and MWNT-TiO₂-400 yielded four peaks at 283.6, 284.5, 286.3, and 288.8 eV, which were assigned to graphitic carbon atoms (46 and 35% for MWNT-TiO₂-300 and MWNT-TiO₂-400, resp.), –C–O, –C=O, and –COO bonds, respectively. The –COO bond was likely formed by the oxidation of MWNT surfaces during the composite synthesis process [30]. On the other hand, for the MWNT-TiO₂-500 and MWNT-TiO₂-600, the corresponding peaks exhibited much lower intensities, were just trace, or were not shown. This again was attributed to the destruction of MWNTs and other

chemical species during the calcination processes at these high temperatures.

Pure MWNT and MWNT-TiO₂ powders calcined at different temperatures revealed different FTIR spectra (Figure 6). For both the pure and calcined nanocomposites, the main absorption peaks were located at 3440 and 1626 cm^{−1}, which were assigned to the O–H stretching vibration of hydroxyl groups and the O–H bending of surface adsorbed water, respectively [31]. For the calcined MWNT-TiO₂ powders, although their intensities differed according to the calcination temperature, other distinctive peaks were observed at low frequency bands <1,000 cm^{−1}. These peaks were assigned to the Ti–O–Ti vibration of the network [32], confirming the presence of TiO₂ in the calcined nanocomposites.

3.2. BTEX Decomposition Efficiencies via MWNT-TiO₂ Nanocomposites.

The as-prepared MWNT-TiO₂ nanomaterials were evaluated for the decomposition of gas-phase BTEX at an IAC level (0.1 ppm). Figure 7 illustrates the average photocatalytic decomposition efficiencies for BTEX determined using the MWNT-TiO₂ unit with two light sources (conventional 8-W black-light and blue LED lamps) under the FR condition of 1.0 L min^{−1}. Under similar operating conditions, the decomposition efficiencies determined using the conventional lamp/MWNT-TiO₂ unit were higher than those of the conventional lamp/Degussa P25 TiO₂ unit, which were reported previously [33]. The mean efficiencies obtained from the conventional lamp/MWNT-TiO₂ unit were 95% for benzene and ~100% for the other target compounds (TEX). Jo and Yang [33] reported the mean degradation efficiencies for BTEX obtained from the conventional lamp/Degussa P25 TiO₂ unit of 56%, 76%, 92%, and 93%, respectively. Consequently, the MWNT-TiO₂ composite revealed superior performance in the photocatalytic decompositions of IAC-level toxic aromatic pollutants to the commercially available reference photocatalyst, Degussa P25 TiO₂. This was attributed to the combined electrical properties and adsorption capacity of the MWNT-TiO₂ composite. MWNTs have a large electron-storage capacity to store photon-excited electrons in MWNT-TiO₂ nanomaterials [25]. This electron-storage capacity would likely retard or hinder electron-hole recombination. In addition, at the interface of MWNT-TiO₂, electrons transfer from the TiO₂ with a higher than Fermi energy level to the MWNT with a lower Fermi energy level to adjust the Fermi energy levels [13]. This electron transfer can result in TiO₂ with an excess negative charge and MWNT with an excess positive charge. Thus, the MWNT would act as an electron sink. Consequently, the formation of this MWNT-TiO₂ junction would extend the recombination times of the photogenerated electron-hole pairs, thereby enhancing the photocatalytic activity of TiO₂. MWNTs also have high adsorption capacity with typical specific surface areas of 200–400 m² g^{−1} [25]. Therefore, MWNTs would assist the TiO₂ powders by concentrating the pollutants and intermediates around the powders followed by subsequent migration of these species to the surface of the photocatalyst

FIGURE 4: Scanning electron microscopy images of MWNT-TiO₂ at four different calcination temperatures (300, 400, 500, and 600°C).

FIGURE 5: X-ray photoelectron spectra of MWNT-TiO₂ at four different calcination temperatures (300, 400, 500, and 600°C).

FIGURE 6: Fourier transform infrared spectra of MWNT-TiO₂ at four different calcination temperatures (300, 400, 500, and 600°C).

via diffusion [34]. Adsorption in MWNTs would occur in the aggregated pores, inside the tube, or on the external walls [25].

Figure 7 compares the decomposition performance of the MWNT-TiO₂ units using the conventional lamp with that using the blue LEDs. The decomposition efficiencies

FIGURE 7: Time-series photocatalytic decomposition efficiencies determined via MWNT-TiO₂ irradiated using two light-source types (conventional 8-W black light lamp and blue-LEDs): benzene (a), toluene (b), ethyl benzene (c), and o-xylene (d).

for BTEX determined using the conventional lamp/MWNT-TiO₂ unit were higher than those of the blue LEDs/MWNT-TiO₂ unit. For the blue-LED/MWNT-TiO₂ unit, the average efficiencies for BTEX were approximately zero, 5, 23, and 28%, respectively. TiO₂ is a semiconductor photocatalyst with a band gap energy of 3.2 eV, meaning that only light with a wavelength ≤ 385 nm can overcome this barrier [35]. Since the conventional lamp and UV-LED exhibit the maximum light intensity at 352 and 380 nm, respectively, both light sources had sufficient energy to promote electrons from the valence band to the conduction band of TiO₂. In general, the activity of the photocatalyst depends strongly on the photon flux on the surface of the catalyst as well as the light irradiation (energy per unit area) [36, 37]. In the present study, the conventional lamp revealed higher light intensity (3.4 mW cm^{-2}) than that of the UV-LED (0.6 mW cm^{-2}). Therefore, the higher decomposition efficiency for the conventional lamp/MWNT-TiO₂ unit was attributed to the combined effects of the lower wavelength (higher energy) with higher light intensity.

Different calcination temperatures might yield different photocatalytic behaviors due to different morphological and electronic properties of MWNT-TiO₂ nanomaterials. Figure 8 represents the decomposition efficiencies as a function of the calcination temperature under the conditions of $\text{FR} = 4.0 \text{ L min}^{-1}$ and conventional UV lamp irradiation. For the target compounds, MWNT-TiO₂-300 and MWNT-TiO₂-400 showed similar decomposition efficiency. The mean efficiencies for BTEX by the MWNT-TiO₂-300 were 32, 70, 79, and 79%, respectively, whereas they were 33, 71, 78, and 78% for the MWNT-TiO₂-400, respectively. On the other hand, when the calcination temperature was increased to 500°C, the decomposition efficiencies decreased to close to zero for both benzene and toluene and to 42 and 44% for ethyl benzene and o-xylene, respectively. When the temperature was increased to 600°C, the decomposition efficiencies were all approximately zero. Higher photocatalytic activities obtained from the MWNT-TiO₂-300 and MWNT-TiO₂-400 were attributed to the combined effects of MWNTs and TiO₂ nanoparticles bound intimately to the MWNT networks, as

FIGURE 8: Time-series photocatalytic decomposition efficiencies (PDEs) determined via MWNT-TiO₂ according to the calcination temperatures: benzene (a), toluene (b), ethyl benzene (c), and o-xylene (d).

confirmed by the morphological and optical properties of the photocatalysts. This assertion is supported by that the carbon materials can accept photogenerated electrons and separate efficiently the charge carriers, thereby enhancing the photocatalytic activity [38–40].

4. Conclusions

This study investigated the feasibility of carbonaceous nanomaterial-assisted photocatalysts calcined at different temperatures for indoor air applications. The MWNT-TiO₂ composites calcined at different temperatures revealed different photocatalytic activities, morphologies, and surface properties. The optical and analytical results showed that for the composites calcined at low temperatures ($\leq 400^\circ\text{C}$) TiO₂ nanoparticles were bound intimately to the MWNT networks. However, no MWNTs were observed when the calcination temperature was increased to higher values. Consistently, the MWNT-TiO₂ composites calcined at the low temperatures showed higher photocatalytic decomposition efficiencies for aromatic hydrocarbons at IAC levels than

those calcined at high temperatures. Moreover, MWNT-TiO₂ exhibited superior photocatalytic performance for the decomposition efficiencies to Degussa P25 TiO₂ under conventional UV lamp irradiations, which was attributed to the combined electrical properties and adsorption capacity for the MWNT-TiO₂ composite. Overall, these carbonaceous nanomaterial-assisted photocatalysts can be applied effectively to indoor air applications, depending on the calcination temperature.

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