Synthesis of TiO$_2$ via Modified Sol-gel Method and its Use in Carbonized Medium-density Fiberboard for Toluene Decomposition

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A solution-type TiO$_2$-based photocatalyst for the decomposition of volatile organic compounds was synthesized using a modified sol-gel method under either alcohol (ethanol or isopropanol) or aqueous conditions. Anatase-type TiO$_2$ was successfully synthesized with additional hydrothermal treatment using either type of medium. However, the aqueous condition for TiO$_2$ synthesis was more convenient for the formation of anatase-type TiO$_2$. Based on X-ray diffraction analysis data, the optimal hydrothermal treatment temperature was 80 °C for anatase-type TiO$_2$ formation; at temperatures below 80 °C or above 90 °C, mostly rutile-type TiO$_2$ was formed. The synthesized anatase-type TiO$_2$ solution was applied to the surface of carbonized medium-density fiberboard (c-MDF). The anatase-type TiO$_2$ on c-MDF showed good maintenance of toluene decomposition performance even after repeated use for 14 weeks.

Keywords: Toluene; Decomposition; TiO$_2$; Carbonization; Medium-density fiberboard

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INTRODUCTION

As industrialization and urbanization have progressed rapidly since the third industrial revolution, pollution of the urban environment has become increasingly severe due to urban concentration and increases in industrial facilities and traffic volumes (Field 2010). In addition, with economic improvements and changes in living and working styles, modern people usually spend more than 90% of their time indoors (US EPA 2010). Therefore, the effect of indoor environments on human health has increased (CDC 2006). Indoor air quality problems have begun to increase with the closure of buildings and the installation of artificial energy-decomposition devices used to improve energy efficiency in various industries (Kim 1999; Spengler et al. 2006). Recently, populations vulnerable to environmental illnesses, such as the elderly, children, and pregnant women, have increasingly suffered from atopy and asthma (US EPA 2010).

In the last decade, nanostructured materials have received great interest for catalysis and other applications because of their unique texture and structural properties (Molinari et al. 2000; Ao and Lee 2004; Guo et al. 2004; Hashimoto et al. 2005). Many studies have focused on metal oxides such as TiO$_2$, SnO$_2$, VO$_2$, and ZnO (Torimoto et al. 1997; Fujishima et al. 2000). Titanium dioxide has received research attention due to its chemical structure and biocompatibility as well as its physical, optical, and electrical properties (Takeda et al. 1995; Doi et al. 2000; Tokoro and Saka 2001; Varghese et al. 2003; Wen et al. 2005). Photocatalytic reactions are widely used for various environmental purification purposes, such as the
decomposition of contaminants in water and air (Andersson et al. 2002; Wahi et al. 2006; Wu and Qi 2007). When TiO$_2$ is used as a photocatalyst, it has three crystal structures, classified as anatase, rutile, and brookite. The low-formation-temperature anatase-type and high-formation-temperature rutile-type are commonly found. Although the two structures have similar tetragonal symmetry, in the rutile crystal structure, the octahedral structures with Ti centers share oxygen atoms at the vertex positions; in the anatase-type, the octahedral structures share edges. Because of these structural differences, the two phases exhibit different physical and chemical properties. To synthesize nanostructured TiO$_2$, the sol-gel process, direct oxidation, chemical vapor deposition, electrodeposition, an ultrasonic chemical method, and a microwave method have been used (Zhang and Gao 2003; Corradi et al. 2005; Wang et al. 2009; Xue et al. 2011; Bazargan et al. 2012; Byranvand et al. 2013; Zhou et al. 2013). Photocatalysts prepared via the sol-gel method are typically applied as coating agents through spin-coating or spraying.

Kercher and Nagle (2002) introduced carbonized boards by pyrolyzing wood-based panels at high temperatures; they were intended for use as fuel cell membranes. The initial carbonized board was prepared at the laboratory scale of approximately 10 cm in size. In 2009, a crack- and twist-free carbonized board was developed by using medium-density fiberboard (MDF), plywood, and wood panels (Park et al. 2009). The physicochemical properties and functionality of carbonized MDF (c-MDF) have been investigated (Zhou et al. 2013; Lee et al. 2014; Lee et al. 2017a,b). The c-MDF can easily remove formaldehyde (a major volatile compound contributing to sick house syndrome) and shows some ability to remove other aromatic volatile organic compounds (VOCs), such as toluene and xylene, from indoor atmospheres (Park et al. 2009).

In this study, to improve the decomposition ability of c-MDF, a nano-sized TiO$_2$ photocatalyst was prepared by using the modified sol-gel synthetic method, and then it was applied to prepared c-MDF to provide photocatalytic function. The anatase-type TiO$_2$ sol-applied c-MDF was then investigated to confirm enhancement of the photocatalytic decomposition ability for toluene.

EXPERIMENTAL

Materials

The MDF (0.64 g/cm$^2$, E$_1$ grade) was purchased from Sunchang Industry (Incheon, Korea).

Titanium tetrapropoxide (Ti-tip) and titanium tetrachloride (TiCl$_4$; DaeJung Chemicals & Metals Co., Ltd., Siheung-si, Gyeonggi-do, Korea) were used as photocatalyst precursors for the synthesis of TiO$_2$. The synthesis was performed in the presence of HCl (1 mol/L, Showa Chemical Industry Co., Ltd., Tokyo, Japan), NH$_4$OH (DaeJung Chemicals & Metals Co., Ltd., Siheung-si, Gyeonggi-do, Korea), NaOH (Duksan Pure Chemical Co., Ltd., Seoul, Korea), isopropyl alcohol (IPA; DaeJung Chemicals & Metals Co., Ltd., Siheung-si, Gyeonggi-do, Korea), and ethyl alcohol (99.5%, EtOH; Duksan Pure Chemical Co., Ltd., Seoul, Korea).

Standard TiO$_2$ (mixture of rutile and anatase types, nanopowder, < 100 nm) was purchased from Sigma-Aldrich (St. Louis, MO, USA).
Methods
Preparation of c-MDF

The MDF, which is a raw material for manufacturing the photocatalytic c-MDF, was cut into samples measuring 130 cm × 260 cm × 1.2 cm (W × L × T) and then wrapped in newspaper and aluminum foil according to Park’s method (2009). The prepared MDF was stacked between graphite plates in a heat resistant box and then placed in an electric furnace. The carbonization program used a heating rate of 50 °C/h and a maximum temperature of 600 °C, which was held for 2 h followed by natural cooling (Park et al. 2009).

Synthesis of TiO₂-sol using alcohols

The Ti-tip was used as a photocatalyst precursor to synthesize the sol-type photocatalyst using alcohol (either EtOH or IPA) as the solvent (Fig. 1). In an Erlenmeyer flask (1 L), 340 g of the selected alcohol and 20 g of Ti-tip were mixed to prepare Solution 1. To prepare Solution 2, distilled and deionized (DI) water (80 g) and concentrated hydrochloric acid (5 g) were mixed in 340 g of alcohol (EtOH or IPA) and placed in a separatory funnel. Solution 2 from the separatory funnel was added dropwise at 60 drops/min to Solution 1 while it was stirred in an ice bath. The mixing of Solution 1 and Solution 2 continued for 3 h with an additional 1 h of stirring. To replace the alcohols with DI water, centrifugation was performed at 6,000 rpm (652 G-force) for 20 min at 10 °C. After decantation, 400 mL of DI water was added to the precipitate, followed by ultrasonic treatment (10 min) for dispersion. The TiO₂ dispersed in the DI water was refluxed at 80 °C for 1 h.

Synthesis of sol-type TiO₂ using water

The TiCl₄ was used as a photocatalyst precursor to synthesize a sol-type photocatalyst under an aqueous condition. Approximately 19 g of TiCl₄ was placed in an Erlenmeyer flask (1 L) and cooled in iced water. The DI water (200 mL) was slowly added dropwise to the cooled TiCl₄ solution to prepare a 0.5 M TiOCl₂ aqueous solution. A 5 M NH₄OH aqueous solution was added dropwise for approximately 10 min to the prepared 0.5 M TiOCl₂ aqueous solution to obtain the TiOH precipitate as a reaction product. To remove Cl ions from the TiOH precipitate, it was washed three times with DI water and the supernatant was removed via...
centrifugation. The conditions for centrifugation were 6,000 rpm (652 G-force) for 20 min at 10 °C. The washed TiOH was dispersed via sonication for 10 min in 200 mL of 5 M NaOH solution. The aqueous solution of NaOH in which TiOH was dispersed was thermally treated at reaction temperatures ranging from 50 °C to 100 °C for 1 h, as well as at room temperature (25 °C). The supernatant was removed through centrifugation. The resulting precipitate was treated in 200 mL of 0.5 M HCl solution at 60 °C for 24 h with occasional shaking. After treatment, the suspension was centrifuged under the same conditions mentioned above. The resulting TiO₂ was subsequently washed with DI water until the pH reached 7.0. The washed TiO₂ was dispersed in 200 mL of DI water through ultrasonication for 10 min (Fig. 2).

**Fig. 2.** Flow chart of sol-type TiO₂ preparation using water

**Crystallinity of TiO₂**

X-ray diffraction (XRD; X'pert Powder; Malvern Pananalytical Ltd., Malvern, United Kingdom) was used to confirm the crystal form of TiO₂. The synthesized sol-type TiO₂ was dried and finely ground in an agate mortar and then placed in a sample holder. The holder was mounted, and the sample was measured at 2θ values from 15° to 80° at 40 kV and 30 mA. All spectra obtained were normalized and then used.

**Microscopic analysis of sol-type TiO₂/c-MDF**

After the synthesis of sol-type TiO₂-treated c-MDF (sol-type TiO₂/c-MDF), a scanning electron microscope (SEM, JSM 6400; JEOL Ltd., Tokyo, Japan) and energy-dispersive spectroscopy (EDS, JED-2300; JEOL Ltd., Tokyo, Japan) were performed to determine the Ti distribution on the surface of the c-MDF. To analyze the particle size of the synthesized TiO₂, a spherical aberration-corrected transmission electron microscopy (TEM, JEM-ARM 200F;
JEOL Ltd., Tokyo, Japan) was used. The sample grid was immersed in a 1/10 diluted TiO$_2$-sol in IPA. The grid was then dried on a hot plate to remove the solvent. Before analysis, the dried grid was pretreated by an ion cleaner (EC-52000IC, JEOL Ltd., Tokyo, Japan) for 10 min. The acceleration voltage used was 200 kV and the lattice resolution was 0.2 nm.

_Toluene decomposition performance_

A sol-type TiO$_2$/c-MDF (300 cm$^2$) was placed in a 20-L stainless steel chamber that was filled with 20-ppm toluene standard gas three times to evaluate the toluene decomposition performance. A Tedlar bag (25-L, TP-25; TRS Environment™, Chesterfield, MI, USA) filled with nitrogen was connected to one of the inlets at the bottom of the chamber. The concentration of toluene in the chamber was monitored at 0 h, 1 h, 3 h, 5 h, 7 h, and 9 h after the chamber was irradiated with ultraviolet (UV) radiation with wavelengths of 360 nm. A 1.0 L sample of air was collected in a Tenax-TA adsorption tube (Supelco Inc., Bellefonte, PA, USA) at a flow rate of 167 mL/min and then analyzed with a gas chromatograph-mass spectrometer (GC-MS, QP2010; Shimadzu, Kyoto, Japan). The analysis conditions are shown in Table 1.

**Table 1. GC-MS and TD Analysis Conditions**

<table>
<thead>
<tr>
<th>TD-20 (Shimadzu, Kyoto, Japan)</th>
<th>GC/MS (QP2010; Shimadzu, Kyoto, Japan)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>List</em></td>
<td><em>Condition</em></td>
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<td>Desorption temperature</td>
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<tr>
<td>Desorption time</td>
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<tr>
<td>Cold trap temperature</td>
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<tr>
<td>2nd desorption temperature</td>
<td>300 °C</td>
</tr>
<tr>
<td>Cold trap hold time</td>
<td>15 min</td>
</tr>
<tr>
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<td>Tenax TA</td>
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<tr>
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<td>Valve temperature</td>
<td>210 °C</td>
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<tr>
<td>Transfer line temperature</td>
<td>250 °C</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

_Sol-type TiO$_2$ Synthesized Using Alcohols_

_Sol-type TiO$_2$ synthesis_

The final concentrations of sol-type TiO$_2$ synthesized using lower alcohols (IPA and EtOH) were 0.71% and 0.72%, respectively. After the preparation of sol-type TiO$_2$ by IPA or EtOH, TiO$_2$ appeared to be well dispersed. However, after standing overnight, precipitates were observed in the TiO$_2$ synthesized using IPA as the solvent, which would impede spraying. The TiO$_2$ synthesized in EtOH remained well dispersed after standing overnight (Fig. 3).

_Crystallinity of sol-type TiO$_2$ synthesized in alcohols_

The X-ray diffraction analysis of TiO$_2$ synthesized using alcohols as solvents showed anatase-type TiO$_2$ in both the solvents. However, the peak width and intensity in each sample
were wide and low, respectively (Fig. 4). Therefore, the crystallinity of TiO₂ may be very low in both sol-type photocatalysts. As previously mentioned in the TEM results, TiO₂ that was synthesized under these alcohol conditions was mostly amorphous in phase.

Fig. 3. Photos of sol-type TiO₂ synthesized in IPA and EtOH after 1 day

Fig. 4. XRD patterns of sol-type TiO₂ synthesized in IPA and EtOH

**Crystallinity of hydrothermally treated sol-type TiO₂ synthesized in alcohols**

The two types of alcohols, IPA and EtOH, used in the reaction were replaced with DI water, and then thermal treatment was conducted under refluxing conditions. As shown in Fig. 5, XRD data indicated that the amorphous form of TiO₂ was transformed into crystalline TiO₂. However, the peak width remained greater than that of the standard TiO₂ used as the standard sample. Therefore, low photocatalyst activity was expected. In addition, the synthesis of a sol-type photocatalyst using alcohols may be less economically efficient because additional processes of water substitution and thermal treatment are necessary.
**Sol-type TiO₂ Synthesized with Water**

*Sol-type TiO₂ synthesis*

The final concentration of the sol-type TiO₂ synthesized in water was 3.11%. In the syntheses using IPA and EtOH, phase separation was observed after TiO₂ preparation, followed by gelation as time passed. However, the sol-type TiO₂ synthesized using water as a solvent showed good dispersity, although some precipitates were observed 10 days after preparation (Fig. 6.).

**Microscopic observation of sol-type TiO₂ synthesized with water**

Figure 7 shows TEM images of TiO₂ synthesized in water. The TiO₂ prepared by hydrothermal treatment at 80 °C showed spherical crystals; TiO₂ that was hydrothermally
treated at 100 °C showed acicular crystals. In general, anatase TiO₂ was spherical and rutile TiO₂ showed rod or needle forms (Fujishima et al. 2000; Hashimoto et al. 2005). The anatase-type TiO₂ was formed by hydrothermal treatment at 80 °C. The TiO₂ treated at 80 °C had an average length of 35 ± 11 nm and a width of 25 ± 12 nm. The TiO₂ treated at 100 °C had an average length of 72 ± 14 nm and a width of 14 ± 5 nm.

![Fig. 7. TEM images of sol-type TiO₂ synthesized in water by hydrothermal treatment](image)

**Crystallinity of sol-type TiO₂ synthesized in water**

During the alkali treatment that followed the ammonia water treatment, the effect of various temperatures on the crystal form changes of the sol-type TiO₂ was investigated. Particles of the sol-type photocatalyst alkali that was treated at room temperature appeared amorphous, similar to those of the photocatalysts prepared using alcohols. From Fig. 8, the amorphous phase of TiO₂ was transformed into a crystalline one with heating applied during the alkali treatment.

![Fig. 8. XRD pattern of sol-type TiO₂ prepared at 80 °C and 100 °C](image)

During treatment at 80 °C, all peaks related to rutile crystals in the XRD data disappeared, with only anatase crystal peaks remaining. With treatment at 90 °C or higher, the
anatase crystal peaks disappeared again and rutile crystals peaks appeared. These results indicated that 80 °C hydrothermal treatment was the optimum condition for synthesizing anatase-type TiO$_2$, which is known to have higher photocatalytic activities. Therefore, the hydrothermal conditions were critical in synthesizing the anatase form of the TiO$_2$ photocatalyst in water. In addition, XRD pattern of TiO$_2$ treated under 70 °C showed similar pattern to 100 °C treated TiO$_2$ (data not shown). Therefore, a mixture of anatase and rutile crystals of TiO$_2$ was formed with treatment at 50 °C to 70 °C. A spherical aberration-corrected TEM was used to observe the crystal lattice of TiO$_2$ obtained from the photocatalyst precursors Ti-tip and TiCl$_4$. The TiO$_2$ was shown to have a hexagonal close-packed structure, which is expected to have a face-centered cubic (FCC) lattice with 001 zone axis. Figure 9 shows the crystal lattice of sol-type anatase TiO$_2$ particles treated at 80 °C. The TiO$_2$ lattice dimension was 0.344 nm to the first point and 0.262 nm to the second point, confirming that the axis was 001 in an FCC lattice. These values were compared with Joint Committee on Powder Diffraction Standards (JCPDS) card values. The synthesized TiO$_2$ from water conditions with 80 °C hydrothermal treatment was thus confirmed as anatase-type through a spherical aberration-corrected TEM observation.

**Fig. 9.** A spherical aberration-corrected TEM data confirming crystal lattice of sol-type TiO$_2$ synthesized in water condition with 80 °C hydrothermal treatment (reference code: 98-020-2242)

**Distribution of sol-type TiO$_2$ on c-MDF**

The sol-type TiO$_2$ synthesized in water with hydrothermal treatment at 80 °C was brushed on the surface of the c-MDF, which was prepared at 600 °C for 2 h. The TiO$_2$ distribution was examined using SEM-EDS. Figure 10 showed the EDS data for Ti, which was distributed over the entire surface of the c-MDF. As shown in Table 2, the surface of the c-MDF was covered by TiO$_2$ with the ratio of Ti to O of approximately 2:1.
Table 2. Atomic and Mass Percentages of Ti, O, and C on c-MDF

<table>
<thead>
<tr>
<th></th>
<th>Mass (%)</th>
<th>Atomic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>6.45</td>
<td>1.72</td>
</tr>
<tr>
<td>O</td>
<td>4.04</td>
<td>3.22</td>
</tr>
<tr>
<td>C</td>
<td>89.51</td>
<td>95.06</td>
</tr>
</tbody>
</table>

Fig. 10. Distribution of Ti (yellow dots) of sol-type TiO$_2$ on c-MDF

**Toluene Decomposition Performance of Sol-type TiO$_2$/c-MDF**

Ordinary c-MDF is known to have low removal performance for aromatic volatile compounds, such as toluene, xylene, and styrene (Park et al. 2009). Figure 11 shows the toluene decomposition performance of sol-type TiO$_2$ synthesized via hydrothermal treatment on c-MDF. The 80 °C-treated TiO$_2$ showed the highest toluene decomposition rate, while the toluene decomposition rate for the 100 °C-treated TiO$_2$ was lower than the 80 °C-treated TiO$_2$. However both specimens of TiO$_2$-treated c-MDF showed higher toluene decomposition rate than the blank samples and the samples that only used c-MDF.

Fig. 11. Toluene decomposition of sol-type TiO$_2$ synthesized by 80 °C and 100 °C treatment on c-MDF and commercial sol-type TiO$_2$ on c-MDF (blank: toluene standard without sample)
In general, anatase-type TiO$_2$ has a high photocatalytic activity because it shows higher oxidizing activity than the rutile structure. However, the 100 °C-treated TiO$_2$, which mainly comprised the rutile phase, also showed moderate photocatalytic activity. According to Wang et al. (2007), rutile-type TiO$_2$ showed good photocatalytic activity at the nanoscale. In this experiment, the synthesized rutile-type TiO$_2$ had an average length of 72 ± 14 nm and width of 14 ± 5 nm. Therefore, nanoscale rutile-type TiO$_2$ also could be used as a photocatalyst, although it was less effective than anatase-type TiO$_2$.

The same samples were repeatedly tested under the same conditions for 14 weeks to examine the reusability and persistency of the toluene decomposition performance of the c-MDF treated with the synthesized sol-type TiO$_2$. The sol-type TiO$_2$/c-MDF decomposed 20 ppm of toluene in the 20-L chamber within 7 h to 8 h in each test (14 times) over 14 weeks; therefore, treated c-MDF could be applied as an interior material to improve indoor air quality (Fig. 12).

![Graph](image)

**Fig. 12.** Persistency of sol-type TiO$_2$-applied c-MDF for toluene decomposition over 14 weeks

**CONCLUSIONS**

1. Sol-type TiO$_2$ photocatalysts (3%) were synthesized using a modified sol-gel method in alcohol (IPA or EtOH) or water. In the TiO$_2$ synthesis, the lower alcohols, such as IPA and EtOH, were unsuitable for the formation of crystalline TiO$_2$. The water condition favored the formation of anatase-type crystalline TiO$_2$.

2. The most important factor in the water synthesis of anatase-type TiO$_2$ was the hydrothermal treatment temperature. The XRD analysis of the TiO$_2$ showed that anatase-type TiO$_2$ could be produced with hydrothermal treatment at 80 °C, while mostly rutile-type TiO$_2$ was formed in hydrothermal treatments at temperatures below 80 °C or above 90 °C.

3. Based on Ti mapping analysis using SEM-EDS, the TiO$_2$ was uniformly distributed on the surface of c-MDF.

4. The sol-type TiO$_2$ on c-MDF showed outstanding toluene decomposition performance (100% degradation of 20 ppm toluene within 7 h to 8 h) with good performance maintenance for 14 weeks.
REFERENCES CITED


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